REDUCTION BEHAVIOUR IN ORE-GRAPHITE MIXTURE IN ARGON AND HYDROGEN-CARBON DIOXIDE GASES
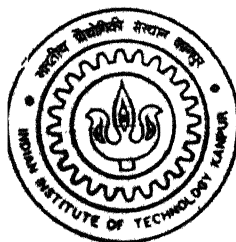
by

Ajay Singh

Department of Materials and Metallurgical Engineering

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

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A Thesis submitted
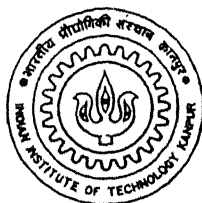
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AJAY SINGH

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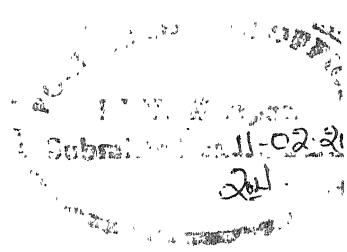
INDIAN INSTITUTE OF TECHNOLOGY KANPUR

FEBRUARY, 2000

CERTIFICATE

It is certified that the work contained in this thesis entitled " *Reduction behaviour in iron ore-graphite mixture in argon and hydrogen-carbon dioxide gases*", by Ajay Singh, has been carried out under my supervision and that this work has not been submitted elsewhere for any degree.

A. Ghosh

Dr. A. GHOSH
Professor
Materials and Metallurgical Engineering,
Indian Institute of Technology, Kanpur
February, 2000

Dedicated to ......

My Mother

and

My Friend late Jayanta Pandey

Acknowledgement

Abstract

In the past there had been fundamental studies on kinetics of reduction of iron oxide by carbon in mixtures of fines of these. The experiments were conducted in either vacuum or inert atmosphere at high temperatures. In recent years, cold-bonded composite iron ore-reductant pellets, consisting of mixture of fines, seem to have considerable future potential as providing one of the alternative iron making routes. These pellets are reduced in industrial furnaces under reactive atmosphere resulting from combustion of carbon/hydrocarbons.

The present investigation has relevance to this. It is a fundamental study on kinetics of reduction of iron oxide in a powder mixture of blue dust and graphite, both under argon as well as under reactive gas atmospheres at 1150K, 1250K and 1300K. The reactive atmospheres were generated by introducing mixtures of H_2 and CO_2 in ratios of H_2/CO_2 equal to 3 and 1.5. Due to water gas shift reaction, they generate gas mixtures consisting of H_2, H_2O, CO and CO_2 at high temperatures in the reduction furnace. Influence of variables, viz. Fe_2O_3/C ratio and size of the sample was also investigated. The experiments were conducted for durations of 600, 1200, 1800, 2400 and 3000 seconds of the sample in the hot zone.

The data on degree of reduction(F) versus time were fitted with polynomial through regression analysis. F Vs.t data for most cases, exhibited highest degree of reduction for inlet gas of H_2/CO_2 ratio equal to 3. For the gas mixture with H_2/CO_2 ratio of 1.5, the F values were lowest in several cases, and were found to be in the middle and even comparable to the gas mixture with H_2/CO_2 ratio of 3, in some others. In argon, the values of F were found to be in the middle in some cases and lowest in others. This may be explained by the fact that, thermodynamically speaking, the gas mixture with H_2/CO_2 ratio of 3,is reducing to wustite. On the other hand, the mixture with

H_2/CO_2 ratio of 1.5 is oxidizing to wustite. However, in some situations, there were departur from this,and attempts were made to explain the same as possible. An interesting finding was tha at 1300K, the oxide got reduced almost completely even under a gas mixture of H_2/CO_2 ratio 1.5.

Furthermore, minimum time to obtain 90 % reduction and maximum value of F (i.e F at = 3000seconds), obtained in this investigation, were compared with those obtained by Deo[1] wit activated char as reductant. Although, it was expected that activated char would reduce faster i view of its higher reactivity, it was not supported by experimental data. Catalytic effect of metalli iron on reactivity of graphite can explain this behaviour pattern.

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Chapter 1

INTRODUCTION

1.1 Introductory

With passage of time,electric arc furnaces are growing in popularity. The principal metallic feed in these furnaces is metallic scrap. In recent times there is a large scale shortage of scrap Worldwide as well as in India. The shortage is going to increase in future. This has led to the growth of sponge iron making processes,because sponge iron is a substitute for steel scrap.

Blast furnace is the principal route of iron making. However due to large capital investment,shortage and cost of metallurgical coking coal as well as environmental pollution during coke-making,there is a World- wide thrust to develop smaller units of alternative method for production of liquid iron in order to supplement blast furnace iron making.

A very promising route of alternative iron making is use of composite pellets of iron ore and reductant(coal,char,coke fines),which are imparted sufficient green strength for handling by cold bonding. Advantages are:

(i)use of cheap raw materials,viz.ore fines,mill scale,non-coking coal fines.

(ii)very fast reduction in mixtures of ore and carbon.

The present study is concerned with reduction behaviour in mixture of iron ore and carbon in various gaseous environment. It is relevant to the alternative iron making through composite pellet

route. Chapter 2 reviews the fundamentals of kinetics of reduction in iron oxide/ore and carbon powder mixture.

1.2 Various alternative iron making processes

Alternative iron making processes are classified into :

(a)Sponge iron making,which is iron making in the solid state. The reduced iron is porous and is known as sponge iron,or DRI(directly reduced iron). Due to high surface area,DRI is prone to rapid re-oxidation and may even be pyrophoric. This poses problem of handling,storage and transport. Hence,many sponge iron making units make dense briquettes by hot pressing of sponge. These are known as HBI(hot briquetted iron).

(b)Bath smelting or smelting reduction,which is a development after 1980s. Here non-coking coal is employed for reduction and heating. Use of oxygen is a must for favourable heat balance. Final reduction of FeO takes place when it is dissolved in liquid slag. Product is liquid hot metal.

Currently,commercially established sponge iron making processes are MIDREX,HyL,Rotary kiln processes and to a very minor extent fluidized bed processes. The only commercially established smelting reduction process is COREX. Several other processes have been at various stages of development. Only the few commercial processes will be described below very briefly. Details are available elsewhere [1].

1.2.1 Sponge iron making processes

(i)**MIDREX process:** The process essentially consists of reducing the iron ore by reformed natural gas in a vertical shaft furnace. It employs a continuous counter current,vertical gas- solid reactor,resembling more or less the stack of a blast furnace.Pellets or lump iron ore are fed into the shaft from the top and the sponge iron,in cooled conditions,is removed from the bottom. The system consists of an efficient off-gas recovery and circulation unit,which makes it economic and environment friendly. Continuous nature of the processes,efficient energy use,amenability to automation and control,as well as high degree of metallization(92-95pct.) and fairly high carbon

content of sponge,have led to wide acceptance of MIDREX process. Largest quantity of sponge is manufactured by this process.

(ii)**Hyl process**: In this process sized iron ore or pellets are reduced by passing reformed natural gas downwards through a retort with a static bed of sized ore or pellets. The overall efficiency of the process is improved considerably by carrying out the process in four stages. The steps are:

(a)preheating the charge and partial reduction by hot gases coming from the primary reduction step. This is also called secondary reduction step

(b)primary reduction,in which the partially reduced charge(from secondary reduction step),is further reduced by strongly reducing gas coming from cooling stage

(c)cooling of reduced charge by fresh gas which itself gets preheated and thereafter will be available for primary reduction

(d)discharging of the sponge iron and recharging of the reactor with fresh charge.

Four reactors are therefore employed and each of the above mentioned operations are staggered in such a way that at any instant of time each of the four reactors is in one of the four stages of the cycle.

(iii)**Rotary kiln processes**: These processes have essentially been designed to carry out reduction using solid reductant like non-metallurgical coal. Both ore and coal are fed as lumps. Additional liquid or gaseous fuel is burnt to generate the working temperature. A long,slightly inclined to the horizontal,slowly rotating kiln is employed to carry out the reduction. The solid charges are fed from the higher end. They travel under gravity aided by rotating motion through several temperature zones. The reduced charge comes out from the other end of the kiln. Reduced and cooled product is screened and the over size is subjected to magnetic separation to obtain clean sized sponge while the non-magnetic oversize is recirculated.

1.2.2   Smelting reduction processes

(i)**COREX process**: It employs lump ore or pellets,or mixture thereof,as raw materials. It is a two-stage process. In the reduction shaft,the ore is reduced upto 93% by a reduction gas generated in the smelting reactor, moving in counter current. Discharge screws convey the DRI

from the reduction shaft into the melter gasifier where final reduction and melting occurs in addition to all other metallurgical reactions. Non-coking coal is charged directly into the melter gasifier. Combustion with oxygen injected into the bath results in generation of a highly reducing gas. Volatile matters of coal also get dissociated into CO and H_2 because of high temperature. The dust coming out with exit gas is separated by a hot cyclone. The top gas is subsequently cooled,cleaned in a scrubber etc.,and is available as valuable export gas for use elsewhere.

(ii)**ROMELT process**: It is not a commercial process yet,but it is in pilot plant stage in Russia. It is being mentioned here in view of interest in India. It is a single-stage bath smelting process. Liquid iron is produced in a molten slag bath reactor using non-coking coal and oxygen. Oxygen is introduced in the reactor at two different levels through water cooled tuyers. The lower level tuyers are submerged in the slag and provide oxygen enriched air blast(40-60%) for gasification of carbon and bath agitation,while upper rows of tuyers supply pure oxygen(95-99%) thereby achieving high degree of post combustion of gases(60-70%). The process requires minimum preparation of raw materials. There is no limitation on size range or moisture content.

1.3 Work plan

In alternative iron making through composite pellet route, the pellets are reduced in reactive atmosphere consisting of CO,CO_2,H_2,H_2O etc. Most of the fundamental studies on mixtures of fines of iron oxide/ore and carbon with and without binder were carried out under inert atmosphere. Hence it was decided that besides argon other gaseous environments will be employed in the present investigation. Due to ease of availability and handling,carbon dioxide and hydrogen were chosen as other gases. A mixture of CO_2 and H_2 undergoes the water gas shift reaction viz.

$$CO_2(g) + H_2(g) = H_2O(g) + CO(g) \tag{1.1}$$
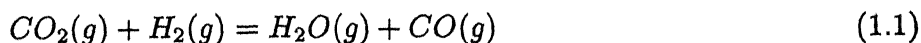
It has been established that this reaction attains equilibrium very fast at high temperature resulting into a known mixture of CO,CO_2, H_2,H_2O.

India has a large reserve of iron ore fines of high grade known as blue dust. There have been studies on composite pellets using blue dust earlier in this laboratory and elsewhere. Hence some

back up data are also available. So it was used for studies here.

Reactivity of carbon is an important parameter. It was decided to employ graphite which has low reactivity. In another study [1] a high reactivity reductant (activated char) was used for comparison.

For proper interpretation controlled cylindrical geometry was employed. Trials were also given with inorganic binders,since organic binders would complicate interpretations. However it was not possible to achieve sufficient green strength for handling.

Influence of the following variables were determined:

(i)temperature

(ii)gas composition

(iii)size of sample

(iv)Fe_2O_3/C ratio

(v)time

The method was to weigh samples before and after reduction. This was supplemented by separate determination of degree of reduction of the oxide.

Chapter 2

LITERATURE REVIEW

The present investigation is concerned with reduction of iron oxide in iron ore-graphite mixture in some gaseous atmospheres. Hence the present literature review will be primarily concerned with this. Most of the fundamental studies have been conducted with intimately mixed fines of iron oxide and carbon.

2.1 Kinetics of reduction of iron oxide/ore and carbon powder mixture

2.1.1 Basic mechanism

The overall reaction may be represented as

$$mFe_xO_y(s) + C(s) = nFe_zO_w(s) + CO(g) \tag{2.1}$$
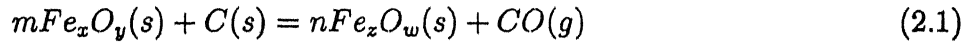
The reason for using symbols x, y, z, w is that there are three oxides of iron, viz Fe_2O_3, Fe_3O_4, Fe_xO ($0.87 < x < 0.955$). It is well established that reduction of iron oxides by carbon occurs as a combination of the following gas-solid reactions. Gasification of carbon:

$$C(s) + CO_2(g) = 2CO(g) \tag{2.2}$$

Reduction of iron oxides by CO, viz.

$$3Fe_2O_3(s) + CO(g) = 2Fe_3O_4(s) + CO_2(g) \tag{2.3}$$

$$Fe_3O_4(s) + CO(g) = 3FeO(s) + CO_2(g) \qquad (2.4)$$

$$FeO(s) + CO(g) = Fe(s) + CO_2(g) \qquad (2.5)$$
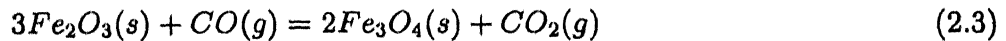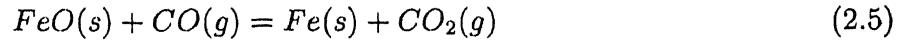
Actually, *FeO* is a non-stoichiometric oxide and be better represented as Fe_xO, where x is a variable ranging from 0.87 to 0.955, depending on oxygen potential and temperature. However in order to avoid complications, it has been represented as FeO in Eqs.(2.4) and (2.5).

Kinetically a solid-solid reaction is expected to be much slower compared to a gas-solid reaction. This is because of the following reasons.

(a) Solid-solid contact area is much smaller than that of gas-solid one.

(b) solid state diffusion is much slower than that of gaseous diffusion.

Therefore,it is more likely that the reduction of iron oxide by carbon will occur via the two component reaction, *viz.* reduction of iron oxides by carbon mono oxide,and gasification of carbon by CO_2. Till late 60s,controversy existed as to whether carbothermic reduction takes place directly or via gasification of carbon in mixture of powder of the two.

Many investigators [2, 3, 4] tried to measure the rates of true direct reduction of iron oxide by carbon at a temperature range of 973-1423°K by continuously evacuating the reaction chamber. They assumed that evacuation of the chamber would result in elimination of product gas phase substantially, thus making the extent of gas-solid reaction negligible. Bankloh et al [2] and Prasad et al [3] used powder mixture of iron oxide and carbon pressed into pellets, and found appreciable rates of carbothermic reduction even upon evacuation of chamber which should eliminate the product gases. Abraham and Ghosh [5] had shown that for a pellet size of around 1cm and pore diameter of the order of 10 μm,the pressure inside the pellet should be at least 10mm of Hg in order to allow flushing of product gases(CO and CO_2) of carbothermic reduction out of the pellet into the evacuation chamber. This is because Knudsen diffusion predominates in pores at low pressures. So in reality, the rate of carbothermic reduction under vacuum observed by investigators, may not be the rate of true direct reduction by carbon but was quite significantly affected by the pressure of the gas in pores.

There have been many observations later which have established that the reduction of iron oxide by carbon in mixture of fines occur via the gas-solid reactions given in Eqs.(2.2),(2.3),(2.4) and (2.5).

2.1.2   Comments on experimental techniques

Weight loss of sample during reduction is due to loss of carbon and oxygen. Measurement of rate of weight loss by thermogravimetry, therefore, cannot yield values of rates of carbon loss ($\dot{W}_c = \frac{dW_c}{dt}$) and oxygen loss ($\dot{W}_o = \frac{dW_a}{dt}$) separately. Therefore, some additional measurement is required.

The product gas is a mixture of CO and CO_2. Its composition depends on rates of $\dot{W}_c$ and W_o. Otsuka and Kunni [6] carried out both thermogravimetry and exit gas analysis by gas chromatography simultaneously to separate W_c, W_o.Abraham and Ghosh [7] achieved the same by exit gas analysis by solid electrolyte cell,and measurement of rate of gas evolution simultaneously. Bandopadhyay et al [8] employed thermogravimetry and gas analysis by gas chromatography.

When a mixture of iron oxide/ore and carbon is introduced into the hot zone of the furnace the reaction begins, but it takes several minutes for the sample to reach the hot zone temperature. This is not only due to finite rate of heat transfer to the sample,but also endothermic nature of reduction by carbon. As a result,a significant fraction of the reaction occurs in non-isothermal condition. Very few investigators measured temperature as a function of time during progress of reaction. Amongst early investigators,Abraham and Ghosh [7] measured temperature continuously.

2.2   Rate control by gasification reaction

2.2.1   Influence of variables

The variables which have been found to influence the reduction rates of iron oxide by carbon are:

- temperature

- nature of carbon

- particle size

- carbon/oxide ratio

- presence of catalyst/inhibitor

It has been established by several investigators that reduction of iron oxides by carbon is dominantly controlled by rate of gasification of carbon(reaction 2.2) [6]-[10]. Again the gasification reaction is primarily controlled by slow chemical reaction step,from evidence such as [11]-[13]

- high activation energy

- catalytic effect of metallic iron, alkalies etc.

- inhibiting effect of CO,some sulphides.

- largely uniform internal reduction.

Temperature also has a pronounced effect on the carbothermic reduction rate. Activation energy generally varies over a wide range starting from 56KJ/mole to 418KJ/mole. It is worth mentioning here that activation energy measured at various degrees of reduction differ quite a bit from stage to stage. On an average,early stage of reduction is characterized by high activation energy(240-300KJ/mole) indicating that it is controlled by gasification reaction,since activation energy for reduction reaction varies between 40-100KJ/mole only (on the other hand the activation energy for gasification reaction ranges between 250-350KJ/mole). The later stage is associated with much lower activation energy probably due to catalytic effect of freshly produced iron.

Particle size is another important factor which contributes significantly to the reduction rate. Workers [9, 10] have found that lowering of carbon particle size enhances the rate. Again dependence of rate of reduction on carbon particle size is an indicator that the overall rate is controlled by gasification. On the other hand Otsuka et al [6] have noticed that decrease of iron oxide particle size also enhance the reduction. They explained this observation by better contact area of particles. They also found that variation of both iron oxide and carbon particle size did not have any significant effect on rate.

Many workers [9, 10, 14] studied the effect of amount of carbon on reduction rate. Rao [9] employed amorphous carbon for reduction of hematite at temperature range of 1123-1290K. They varied the Fe_2O_3/C ratio from 1:1.5 to 1:9 and found that higher proportion of carbon enhanced the reduction rate markedly. For example he found that at 1280K, the time for 50% reduction decreased from 35 to 10 minutes when Fe_2O_3/C ratio increased from 1:1.5 to 1:9

2.2.2   Influence of CO on rate of gasification of carbon

Carbon monoxide has pronounced retarding effect on the rate of gasification of carbon in CO_2. Turkdogan and vinters [12] made extensive measurements on this system. Their results on the effect of temperature and gas composition using CO-CO_2 mixtures at 1atm. on the rates of gasification of coconut charcoal and graphite are shown in Fig.2.1 and Fig.2.2 respectively as semi log plots.

Carbon monoxide is a reaction product as well as its retarding effect had been known. It has been a subject of study by physical chemists from 1930s. Reifs [11] mechanism for surface chemical reaction step was accepted by Ergun [15] with minor modification, and a rate equation was proposed. It was based on Langmuir-Hinshelwood mechanism of adsorption-cum-chemical reaction on solid surfaces, and is as follows.

(1) Reversible oxygen exchange at carbon surface:

$$CO_2(g) + C^| \rightleftharpoons^{K_e} CO(g) + C^{|O}$$
(2.6)

where $C^|$ refers to free surface sites and $C^{|O}$, that of sites with adsorbed oxygen atom. K_1 and K_2 are forward and backward rate constants.

(2) Irreversible gasification of carbon:
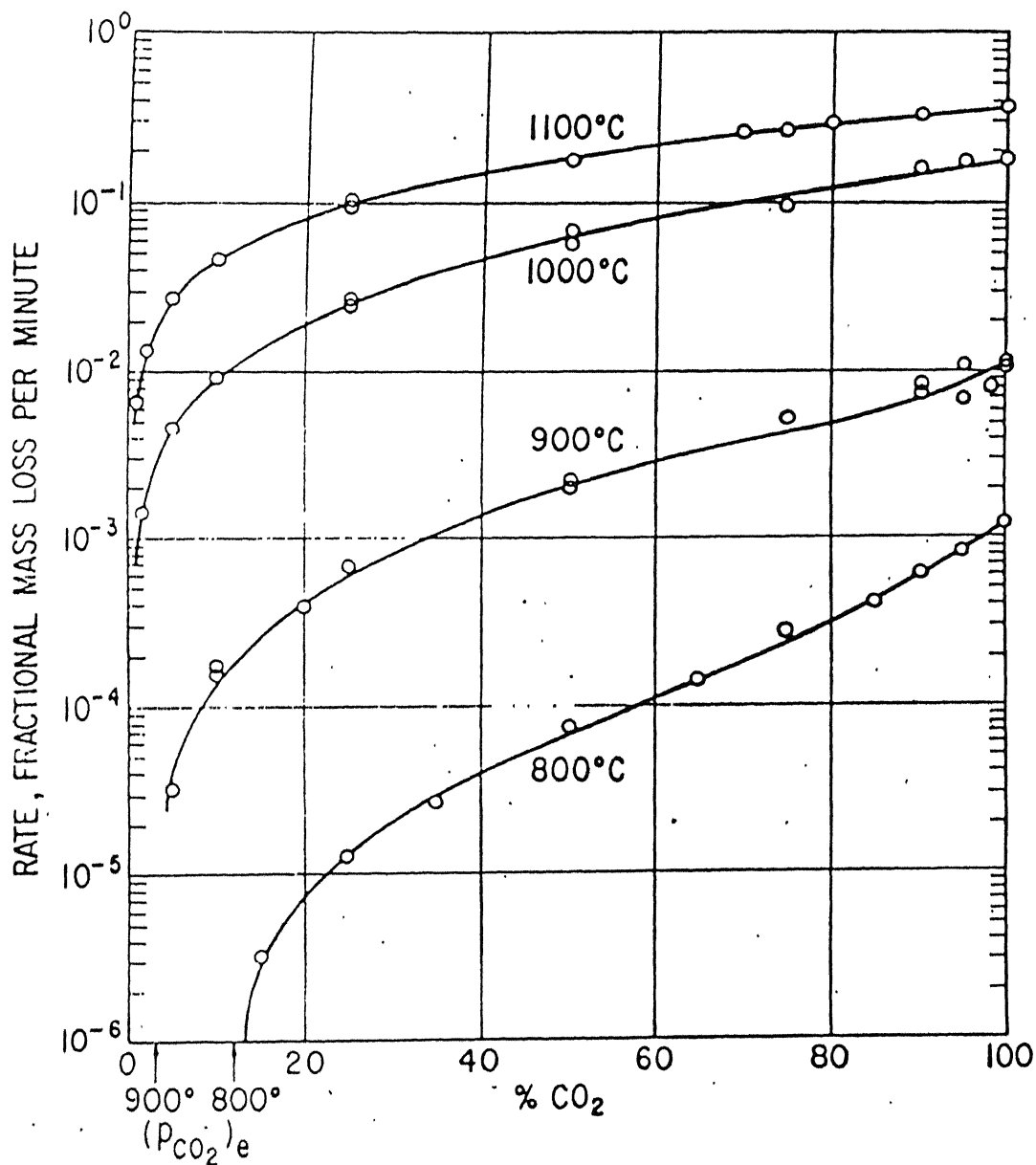
Figure 2.1: Effects of temperature and gas composition on the rate of oxidation of coconut charcoal granules ($\approx$0.5mm dia.) in CO_2-CO mixtures at 0.96 atm total pressure.[12]
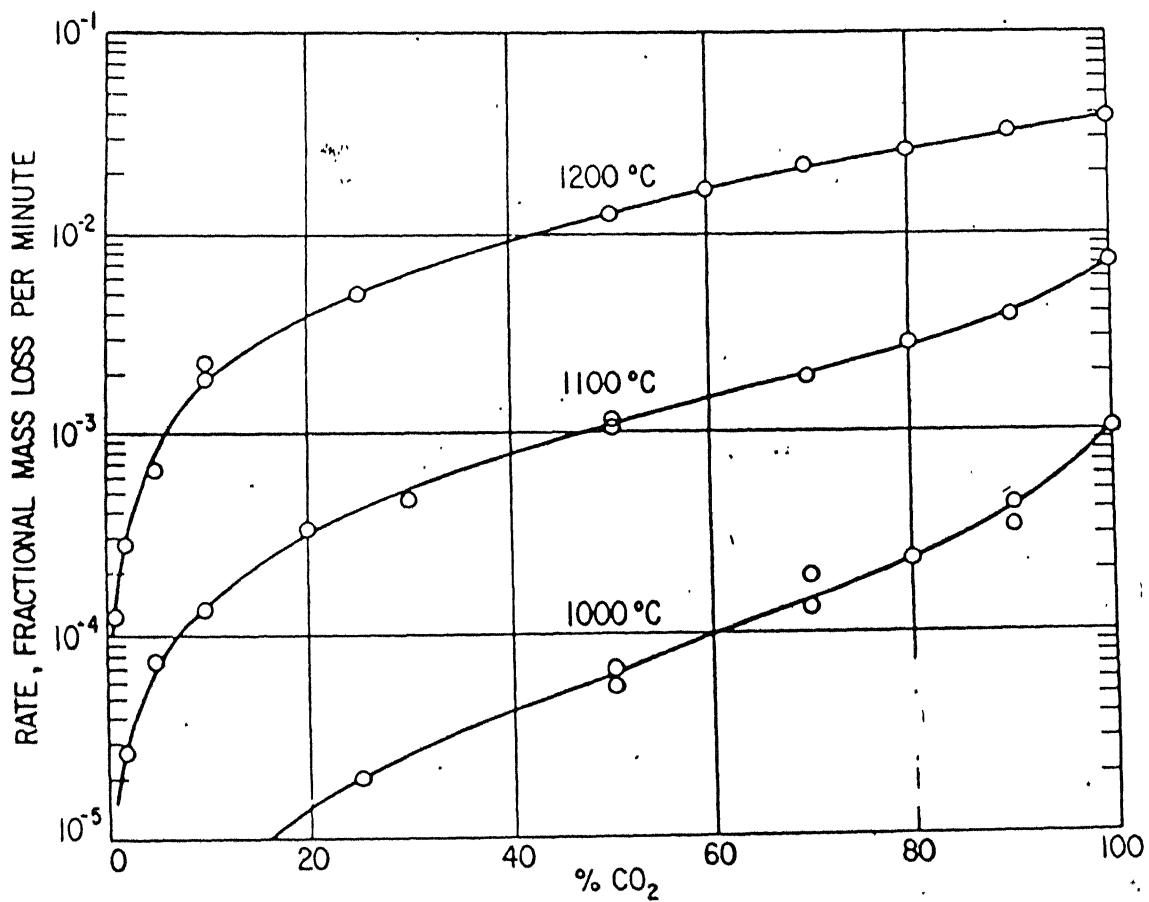
Figure 2.2: Effects of temperature and gas composition on the rate of oxidation n of electrode graphite granules ($\approx$0.5mm dia.) in CO_2-CO mixtures at 0. 96 atm total pressure [12]

$$C^{|o} \rightarrow CO(g) + C^{|} \tag{2.7}$$

On the basis of the above, Ergun [15] proposed the following rate equation for gasification of carbon

$$rate(r) = \frac{I_1 p_{CO_2}}{1 + I_2 p_{CO} + I_3 p_{CO_2}} \tag{2.8}$$

where I_1, I_2, I_3 are temperature dependent constants. Actually

$\frac{I_3}{I_2} = K_e$

where K_e is the equilibrium constant for the reaction . Rao and Jalan [13] later tried to show that even I_2 and I_3 are independent of nature of carbon. However Turkdogan and Vinters [12] questioned reifs mechanism and proposed their own mechanism of surface reaction again assuming rate control by slow surface chemical reaction. However it is Erguns equation which received wider acceptance. Upto 1980s or so it was generally assumed that the gasification reaction is dominantly chemically controlled below 1100°C and particle size of less than 1cm.

However recent findings have questioned both of these [16]. Bandopadhyay et al have demonstrated that there is significant heat and mass transfer limitation in gasification of graphite and coconut char especially the later. They evaluated chemical rate constants(K_c) for gasification in CO_2. For example at 1280K were found to be 1.75×10^{-4} and 95×10^{-4} for graphite and coconut char respectively. The high reactivity of coconut is due to high specific pore surface area as compared to that of graphite. In some recent studies Bandopadhyay et al[16] and Wu et al[17],questioned the validity of the mechanism behind Erguns equation.

2.2.3 Catalysis of gasification reaction and carbothermic reduction by metallic iron

It has been established that gasification reaction is catalysed by metallic iron,alkalies etc. On the other hand CO,some sulphides etc. inhibit the reaction. Turkdogan and Vinters [18] studied the rates of gasification of iron impregnated graphite granules(0.01 to 2.1% Fe) in CO-CO_2 mixtures at temperature range of 973-1273K,and at pressures of 0.03 to 1 atmosphere. They also carried out

gasification of iron-impregnated coconut char and coke. They observed that even with less than 0.01% iron,the rate of reaction of graphite in CO-CO_2 gas mixture at 973-1273K increased by a factor of 2000. Use of 2% impregnated iron enhanced the gasification rate at 1073K by a factor of around one million.

On the other hand Mehrotra and Sinha [19] also studied influence of iron powder on the rate of gasification reaction. They mixed 0-15% iron with carbon black for gasification in carbon dioxide atmosphere in the temperature range of 1073-1273K. They observed only 2.5-3.0 times rate enhancement with 15% iron which is insignificant as compared to what was reported by Turkdogan et al. The reason for such a large difference was that Turkdogan et al[18] impregnated iron in carbon as a result of which iron atoms got incorporated into the structure of carbon and were finely disseminated at molecular level resulting into a very large Fe-C contact area. On the other hand Mehrotra and Sinha [19] employed a mechanical mixture of iron and carbon resulting in a very small contact area than that of Turkdogan.

Alam and Debroy [20] made very comprehensive study on gasification of coke in carbon dioxide using KCN,K_2O_3,KOCN as catalysts. They observed that potassium bearing compounds enhanced the rate quite significantly.

Abraham and Ghosh [7] made investigations into the rates of reaction of porous and dense pellets of ferric oxide with graphite powder. The distance of separation between the oxide pellet and graphite powder was varied from 0 to 1.6cm. The temperature of reaction ranged from 1153-1280K. The flow rate and composition(CO/CO_2 ratio) of the product gases were measured by a capillary flow meter and a solid electrolyte oxygen sensor,respectively. Auxiliary experiments with powder mixture of the two reactants as well as with mixtures of graphite powder and tiny pellets of ferric oxide were also undertaken.

The solid electrolyte sensor was continuously giving values of oxygen potential in the product gas mixture at reaction temperature. Assuming CO-CO_2-O_2 equilibrium p_{CO_2}/p_{CO} ratios could be calculated. The flow meter provided the total flow rate of CO and CO_2 product gas. From these data rates of oxygen loss(-W_o) and carbon loss(-W_c) as a function of time were calculated. The total quantity of oxygen removal from the oxide at any instant of time was calculated by numerical

integration by the following equation

$$\Delta W_o = -\int_0^t \dot{W}_o dt \qquad (2.9)$$

From these data the degree of reduction of oxide could be determined.The rate Vs. % reduction curve in powder mixtures as well as in mixtures of tiny pellets of ferric oxide with graphite powder exhibited two regions. Fig.2.3 presents a rate Vs. % reduction curve for powder mixture of ferric oxide and graphite for experiments by Abraham et al [7]. In mixtures of iron oxide and carbon,the reduction is broadly stagewise viz. $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow Fe_xO \rightarrow Fe$. Metallic iron starts forming at around 25-30% reduction. The rates were controlled by gasification reaction and they were higher in the second region than those in the first presumably due to catalytic effect of reduced metallic iron. There was an appreciable lowering of activation energy in the second region as well. These confirm to the findings of Otsuka and Kunii[6] who first attributed it to the catalytic effect of reduced metallic iron in the second region.

Fruehan [10] made investigations to determine the rate of reduction of reagent grade Fe_2O_3 and prepared FeO by coconut char ,coal char and coke, in an inert atmosphere within the temperature range 900-1200°C. He found that the iron formed by the reduction does not significantly catalyze the oxidation of carbon. It was attributed to high reactivity of the char.

Bandopadhyay et al[8] carried out carbothermic reduction experiments with two types of material configurations viz. iron oxide and coconut char powder mixture,and iron oxide micro pellets mixed with coconut char powder. Reduction experiments with powder mixture were performed at 1078,1145,1208 and 1284K where as experiments with micropellets were conducted at 1145,1210,1235 and 1284K. Rates of weight loss were measured as a function of time using a thermogravimetry set up. Product gas analysis was carried out using gas chromatography to separate rates of carbon loss and oxygen loss. For them although the catalytic effect was not significant,but the effect was observed for both the systems (Fig.2.4). This may be explained in terms of more sintering at higher temperatures and mass transfer resistance.
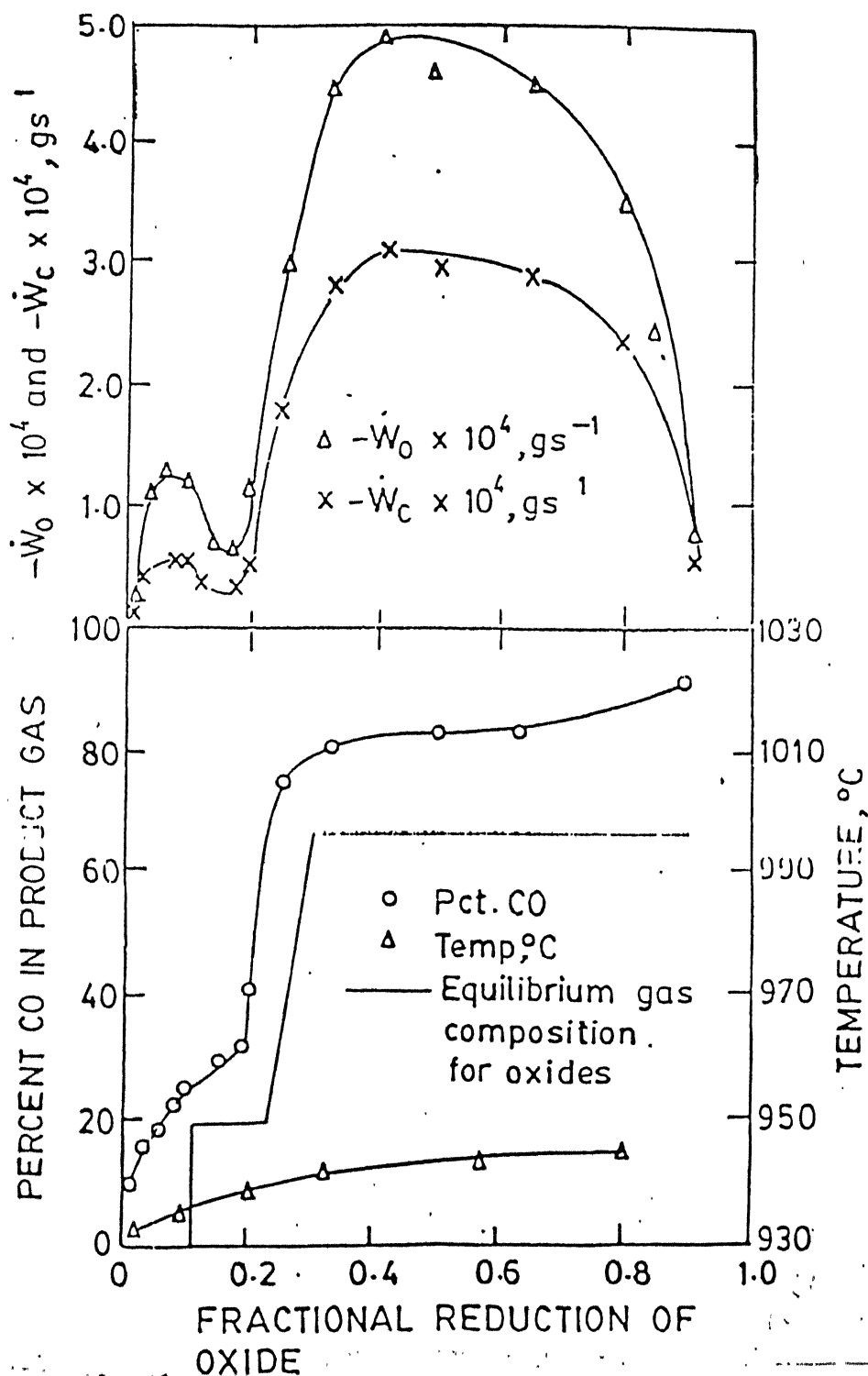
Figure 2.3: $-\dot{W}_o$, $-\dot{W}_c$, temperature, and composition of product gas as a function of fractional reduction of oxide for powder mixture of Fe_2O_3 and graphite

[7]
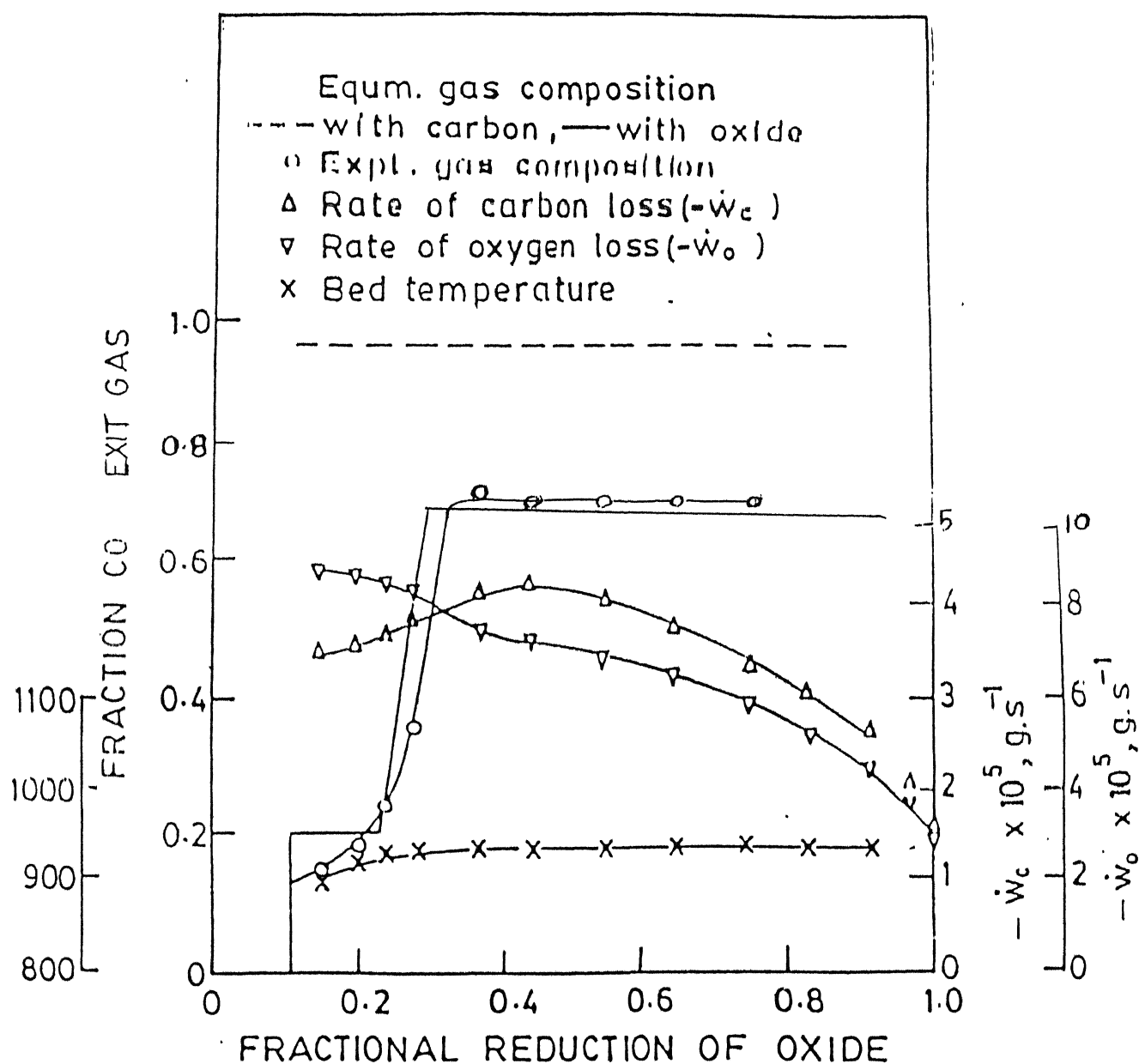
Figure 2.4: Variation of rates, exit gas composition and bed temperature with fractional reduction of oxide in powder mixture of Fe_2O_3 and coconut char.[8]

2.2.4   Quantitative analysis of carbothermic reaction

Srinivasan and Lahiri[26] were the first to carry out theoretical quantitative analysis on reduction of iron oxide by carbon. Erguns equation for gasification reaction was accepted and pore diffusion was considered. They tried to predict minimum temperature below which the gasification reaction rate was so low that it was unable to generate sufficiently high p_{CO} for reduction of iron oxides, of course variables such as carbon reactivity would influence this temperature. Below this temperature only direct reduction by carbon would be possible

Rao and Chuang[27] did mathematical modeling on reaction between fine particles of ore and carbon mixture. The model considered surface reactions,Knudsen diffusion through pores and viscous flow of gases through pores due to pressure gradient generated. Tien and Turkdogan[28] also considered rate control by gasification reaction as well as by diffusive and viscous flow of the reaction products,viz. CO_2 and CO through packed bed due to pressure gradient. However their mathematical formulation was different from that of Rao and Chuang since the later predicts a pressure build up of several atmospheres inside the bed. This is impossible since the bed will rupture and particles thrown away under such excessive pressure. Actually Tien and Turkdogan model is more appropriate since in these pore size ranges,molecular diffusion rather than Knudsen diffusion dominates.

Tien and Turkdogan[28] found that the experimental rate data for reduction of FeO by coconut char by Fruehan [10] agreed with the rate of gasification of coconut char, measured by Turkdogen and Vinters [12].

As stated earlier that two rate equations for intrinsic chemical reaction for gasification of carbon had been proposed,one by Ergun[15] and the other by Turkdogan et al[12]. The carbothermic reduction experiments by Abraham and Ghosh[7] have also been briefly reported earlier. Assuming rate control by gasification step, they tried to correlate rate of gasification of graphite with the rate of carbothermic reduction of Fe_2O_3 pellets by graphite powder kept in separation. However they came up with an anamoly by an order of magnitude between the two. Tiwari et al[29] subsequently measured gasification rates of graphite in CO_2 and CO-CO_2 mixture by Cahn automatic electrobalance and found that their experimental data were not agreeing with equations either of Ergun or

Turkdogan et al. Fig.2.5 shows this as normalized rate parameter(Y) Vs. gas composition.

Employing their own gasification rate data, Tiwari et al[29] showed that they were getting good agreement with their calculations and experimental data of Abraham et al (Fig.2.6). The figure also shows poor agreement between original calculations by Abraham et al on the basis of Erguns equation. Bandhopadhyay et al [8] also employed their own experimental data of gasification as well as reduction in iron oxide micropellet-coconut char mixture and obtained reasonable agreement between the two. There have been some recent mathematical modeling and quantitative analysis on reactions of ore-coal mixtures. These will be reported in sec.2.3.4 later.

2.3   Alternative iron making processes through composite pellet route

Deo[1] has reviewed recent literatures on alternative iron making. This review shall be restricted only to composite pellets. The term "composite pellet" in this context means pellet containing mixture of fines of iron bearing oxide and carbonaceous material (coal,coke,char), which has been imparted sufficient green strength for subsequent handling by cold bonding technique. The should have sufficient strength to withstand high temperature and stresses in reduction furnaces.

2.3.1   Advantages of composite pellets are as follows

(i)Since the carbonaceous reductant is in intimate contact with ore fines,reduction is very fast. Laboratory studies have indicated residence time 10-15 minutes at a temperature of 1100° or so as sufficient to result into a degree of metallization above 90-95%. Trails in rotary kiln furnace have found a decrease of residence time by a factor of 6 to 8 upon use of composite pellets.

(ii)Iron ore fines are generated in mines due to mechanized mining,and else where due to crushing,grinding,beneficiation etc. The fines are cheaper than lumps. Moreover,dumping of fines at mine site poses environmental problems. Therefore mines around the world are insisting that iron makers are to buy both lumps and fines. Agglomeration by sintering cannot generally process less than 0.15mm fines. Traditional pellet making is costly due to need of heat hardening in furnace
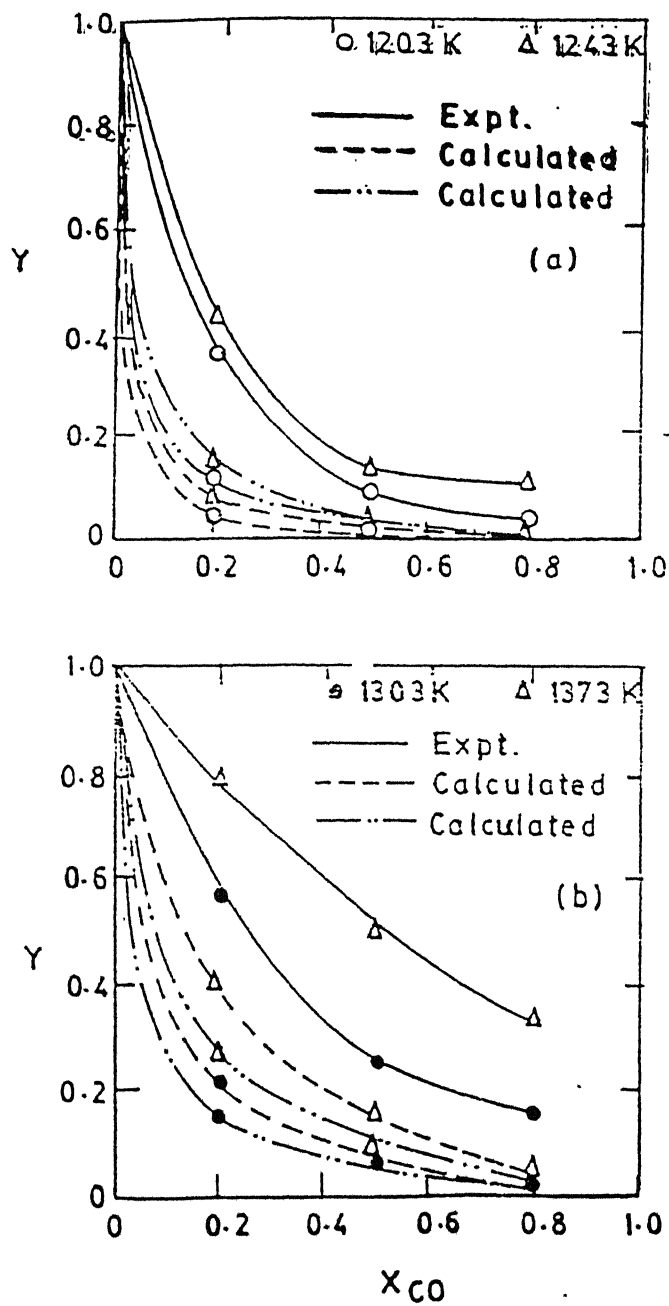
Figure 2.5: Variation of Y with gas composition in CO_2-CO mixture; -experimental(Tiwari et al,1992), —calculated(Rao and Jalan, 1972), .. calculated(Turkdogan and Vinters, 1970).[29, 13, 12]
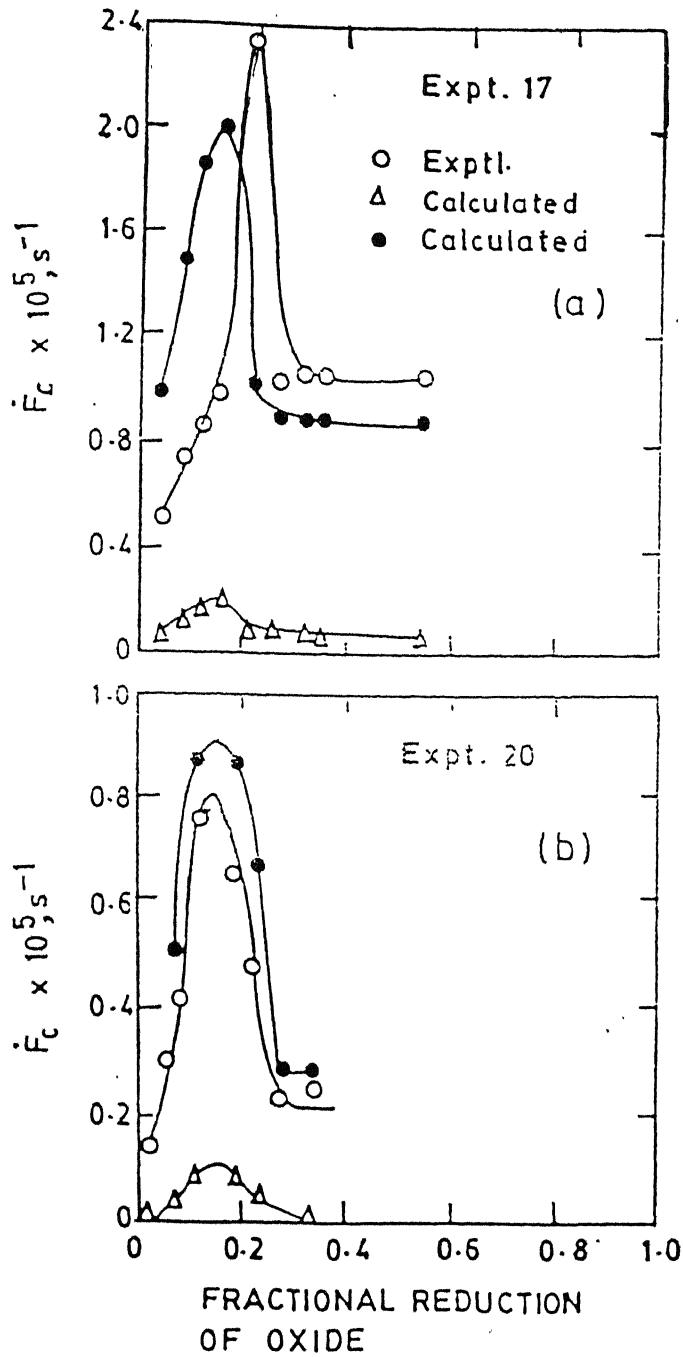
Figure 2.6: Plots of $\dot{F}_c$ against fractional reduction of iron oxide for experiments 17 and 20 of Abraham and Ghosh(1979), •- calculated (Tiwari et al, 1992), $\triangle$- calculated (Abraham, Ph.D thesis, 1976).[29, 46, 7]

at a temperature of 1200-1300°. Cold bonded composite pellets do not require heat hardening and hence constitute a potential alternative route for utilization of ore fines.

(iii) Cold-bonded composite pellets also utilize cheap and readily available reductants such as coal breeze,coke breeze, coal char fines,wood char fines.

2.3.2 Disadvantages of composite pellets

Disadvantages of composite pellets are primarily economic. High cost items are

(i)cost of binder

(ii)cost of grinding.

Research workers [22, 23] have prepared composite pellets with various organic as well as inorganic binders. Starch-based binders, dextrine,molasses and oil slush are some of the organic binders. Bentonite,cement,quicklime,lime and silica etc. have been employed as inorganic binders. Organic binders are costlier than common inorganic binders such as bentonite,but are capable of giving higher dry strength[24].

Experiments carried out by Dutta and Ghosh [42] shows that much higher strength could be achieved with -325 mesh size as compared to -100 mesh. But that would increase grinding cost. Experimental observations have shown that a dry strength above 150N per pellet could be achieved with inorganic binders,only if some cement is used along with lime etc.

In early trials,efforts were made to use composite pellets in blast furnace,cupola and rotary kiln [24, 25]. This required high strength and consequent use of costly binder and pellet making procedure. Hence it turned out to be uneconomic. These efforts have been abandoned now. The current approach recognizes that we have to be satisfied with low strength,cheaper pellets. The reduction is to be carried out accordingly.

2.3.3 FASTMET PROCESS

Griscom and Wood[30] had reviewed the FASTMET process, which has been developed by Midrex and its parent company Kobe Steel Limited, it uses iron ore concentrate and a carbon bear-

ing reductant such as coal to quickly and efficiently produce direct reduced iron. Process equipment is primarily of established designs which have been proven through many years of industrial service. Plants can be designed to produce from 150,000-450,000t/y of FASTMET iron. Because of technical simplicity and attractive economics, the FASTMET process has aroused world wide industry attention as an alternative iron source.

In the FASTMET process(Fig.2.7),iron ore concentrate,which has been ground to proper size(approximately 80 percent minus 74 microns[minus 200 mesh]or smaller), is received and stored at the plant for subsequent use. Lump coal or another solid reductant in lump form is reclaimed from storage and conveyed to a bowl or roller type mill to be pulverized to approximately 80 percent minus 74 microns(minus 200 mesh). The pulverized reductant and iron ore fines are intimately mixed with a binder,such as bentonite or a commercially available organic material,before being conveyed to a balling drum or pelletizing disk to produce green pellets approximately 17-20 mm in diameter.

Green pellets flow from the pelletizer to a low temperature(120°C) belt type drier where moisture is removed. The drying process increases pellet strength somewhat and eliminates the drying load which would otherwise be transferred to the rotary hearth furnace. In addition,dry pellets are less susceptible to breakage,which could occur if wet pellets were exposed to the very high temperature inside the RHF.

Dried pellets are transferred directly to the RHF where they are layered one pellet deep on the solid hearth. Burners located above the hearth provide heat to raise the pellets to reduction temperature of approximately 1250-1350°C. The burners are fired with natural gas,fuel oil,or pulverized coal to supply a portion of heat requirements. The remainder of the heat is supplied by combustion of the volatiles which are liberated from the reductants as the pellets are heated.

Because of very high reaction temperature compared to the other direct reduction process(typicall no more than 900°C to prevent sticking in packed bed-type reduction furnaces) and the intimate mixing of the iron ore and reductant,the residence time in RHF is only 6-12 minutes. Furnace residence time depends on the reactivity of the iron ore and reductant and the desired conversion of iron ore to metallic iron.
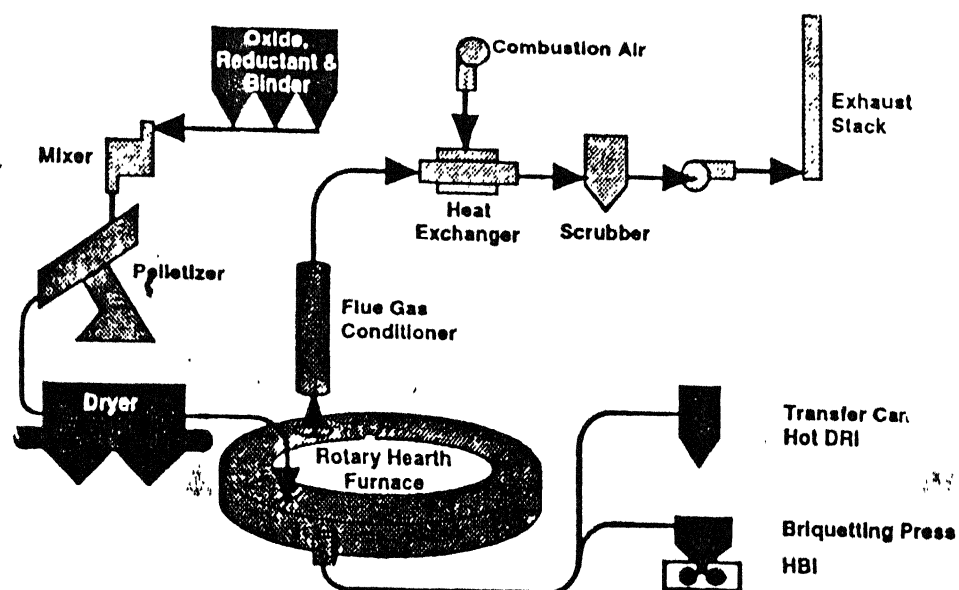
Figure 2.7: Schematic representation of FASTMET process.[30]

The hot, reduced iron is partially cooled to about 1000°C by a water cooled discharge screw and flows by gravity to either a briquetting system to produce hot briquetted iron or into a transfer device to be conveyed hot to an adjacent iron or steel making furnace. Briquettes are produced hot and then cooled if the product is to be stored or shipped to an off-site user.

Based on simulator results FASTMET iron can be metallized upto 95% with reasonable residence times and unit consumptions. Carbon content between 1 and 6 percent,and the level of metallic residual elements(i.e.,copper chromium nickel,molybdenum and tin) will be very low using most iron ores.

As with the gas-based direct reduction processes,the quality of FASTMET iron will be greatly influenced by the chemical purity of the iron ore. However FASTMET iron will be effected by the use of coal as a reductant because gangue elements in the coal remain in the product.

Fixed carbon is what actually performs the reduction function in the FASTMET process. Volatile matter is liberated during heating and is combusted to provide a portion of heat required for the process. Therefore ,the fixed carbon content of the reductant is very important while the volatile matter content is less important from an energy and reductant standpoint. Low fixed carbon means reductant is required,as the amount of reductant is directly related to the fixed carbon content. Low fixed carbon reductant results in lower productivity because more reductant and less iron ore are required in the feed blend. Moreover,if low fixed carbon is combined with high volatile content,more volatiles can be present than can be effectively used in the process. This results in lower energy efficiency and higher off-gas emissions. High volatile content may also result in breakage of pellets during heating because of rapid release of volatile matter from the pellets.

2.3.4   DRyIron process

Rinker and Fredette[31] have reviewed the above mentioned process. The process was developed specifically to process high grade iron ore fines that are typically screened and rejected at both the mine and at the gas based pellet processing facilities. The process is based on heating a solid mixture,but instead of producing a wet green pellet and drying the pellet to a strength acceptable for material handling,Maumee research and engineering,Inc. has refined the art and patented a

binderless dry briquette that eliminates the thermal drying traveling grate associated with the pelletization approach. Coke breeze or non-metallurgical coal and iron ore fines or iron oxide waste materials are intimately mixed and agglomerated into compacts. The compacts are then heated radiantly in a rotary hearth furnace and elevated to the carbon and iron oxide reaction temperature producing metallic iron in the briquette and releasing both carbon monoxide and carbon dioxide. The overall, ideal stoichiometric reaction is as follows

$$2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2 \tag{2.10}$$

The benefits to be derived through the application of this process is,all the energy required for the process can be derived either by a combination of a coal and natural gas or fuel oil. The benefits of converting the virgin iron oxide into DRI lie primarily with the simplicity of the one step thermal process. It does not, as in natural gas based processes,require a pelletization plant,a gas reforming plant, and a reaction vessel incorporating a high level of in process inventory. The simplified DRyIron process capital and operating costs facilitate the production of competitively priced high quality iron units. The short in process residence time has untold advantages when it comes to process flexibility,low in-process inventory,low raw material inventory requirements,and quicker response to maintenance needs.

2.3.5   Fundamental kinetic studies on composite pellets

The reactions in iron ore-coal system are only a few [Eqs(2.2-2.5)]. However there are other reactions and processes in composite pellets, especially in pellets containing coal. During reduction of iron ore-coal composite pellets,volatile matters evolve due to pyrolysis of coal. Decomposition of hydrocarbons at high temperatures and gasification of carbon by CO_2 and H_2O are other reactions leading to the formation of CO and H_2. Pyrolysis of coal also generates reducing gases such as hydrogen and carbon monoxide,besides leaving carbon residue. So the reduction of iron oxide is partly due to reaction with these reducing gases besides that with carbon.

The amount and composition of volatile matters evolved depend on the type of coal,size of coal,and the conditions prevailing in the reaction chamber. A series of consequitive and parallel

reactions occurs during pyrolysis of coal. Although most of the uncombined water is driven off below 375K, this water is not completely removed until the temperature reaches around 575K. Significant devolatilisation does not start until a temperature of 625 to 675K is attained.

there are two stages of devolatilisation of coal

(i)primary devolatilisation at 625 to 875K

(ii)secondary devolatilisation above 875K.

Tar and gases evolve during the primary devolatilisation,while only gases(mainly H_2 and CO) are evolved during secondary devolatilisation. Coal undergoes a series of complex physical and chemical changes upon heating. Products formed during devolatilisation of coal include tar,hydrocarbon liquids,hydrocarbon gases,CO_2,CO,H_2,H_2O etc.

The reduction of composite pellets occurs non-isothermally as it starts during heating. Some published literature [32, 33] on the so called isothermal studies of composite confirms that a significant fraction of reduction actually takes place initially while the sample temperature rises(approximately 10-15 minutes or so). In this context non-isothermal kinetic study of composite pellet has certain advantages,since here temperature rise can be controlled as desired.

Cypress and Soudan-Moinet [34] studied the influence of presence of iron oxides on coal pyrolysis and also studied the relationship between the release of volatile matter from coal and reduction of iron oxides. They heated samples from room temperature to 1273K at the rate of 3.2Kmin^{-1}. They found that in the primary devolatilisation zone,the weight loss of the coal-magnetite mixture was attributable to only the coal devolatilisation. Magnetite was not reduced below 873K. Between 673 and 823 K,Fe_2O_3 was reduced to Fe_3O_4, with losses of water and some CO_2. In the secondary devolatilisation zone,the reduction of iron oxides decreased percentage of H_2 and increased those of CO,H_2O,and CH_4. these investigators concluded that hydrogen plays an important role in the reduction of iron oxides below 1073K.

In non-isothermal kinetic studies of Dutta and Ghosh [35] the rate of reaction was monitored by passing argon gas with known flow rate through the reaction chamber containing composite pellet. The sample temperature was raised approximately at constant rate from room temperature

to 1273K at two rates(viz.in 48 mins and in 96 mins.) reproducibly. The composition of exit gas was analyzed by gas chromatograph at several intervals of time. Gases analyzed were H_2,CO,$CO_2$and CH_4. They employed Bachra and Huter non-coking coals and their chars.

Fig.(2.8) shows the rates of evolution of various gases as function of temperature for:

(i)ore-coal pellet,and (ii)devolatilisation of coal.

CO evolution generally started above 700K,and peaks were observed between 1050 and 1250K,the percentage of CO being as high as 40. Reduction of iron oxide by carbon generates both CO and CO_2. The reaction becomes significant only above 1100K. Therefore the reduction of Fe_xO to Fe by carbon is the likely reason for the enhanced CO content of evolved gas in experiment with composite pellets. For hydrogen evolution the peaks appeared at 1000K to 1100K for ore-coal pellets. This was higher than the temperature range(800 to 850K),observed in devolatilisation of coal. The likely explanation is that a significant fraction of H_2 is used up for oxide reduction in temperature range of 800 to 1100K. Therefore in the composite pellet,the peak height of H_2 was much lower,as well as shifted to a higher temperature.

Investigations by Dutta and Ghosh [35] also led to the conclusion that a significant quantity of oxygen loss as CO,CO_2,H_2O is due to extraneous sources. This was presumed to be strongly chemisorbed and chemically bonded H_2,CO_2 on coal and binder surfaces. These evolve at high temperature,and to some extent would react with carbon to form H_2 and CO as well. The H_2 and CO,in turn, would contribute to reduction of iron oxides. Hydrogen evolution in ore-char composite pellets was also significant and can only be explained this way.

Quantitative estimations on the basis of materials balance of experimental data indicated such extraneous H_2O and CO_2 as approximately 10 pct. of pellet weight. It is to be mentioned here that the pellets in this investigations were prepared by autoclaving. This is held responsible for such high retention of chemically adsorbed/bonded H_2O and CO_2. It is not expected to be so high in non-autoclave route of pellet preparation, as confirmed by the recent work of Lawania [36].

For iron ore/oxide-carbon system,only product gases are CO and CO_2. Hence the procedure outlined earlier are theoretically correct for determination of degree of reduction(F) for the above. For composite ore-coal pellets other gases also evolve. Hence, the situation is more complex and
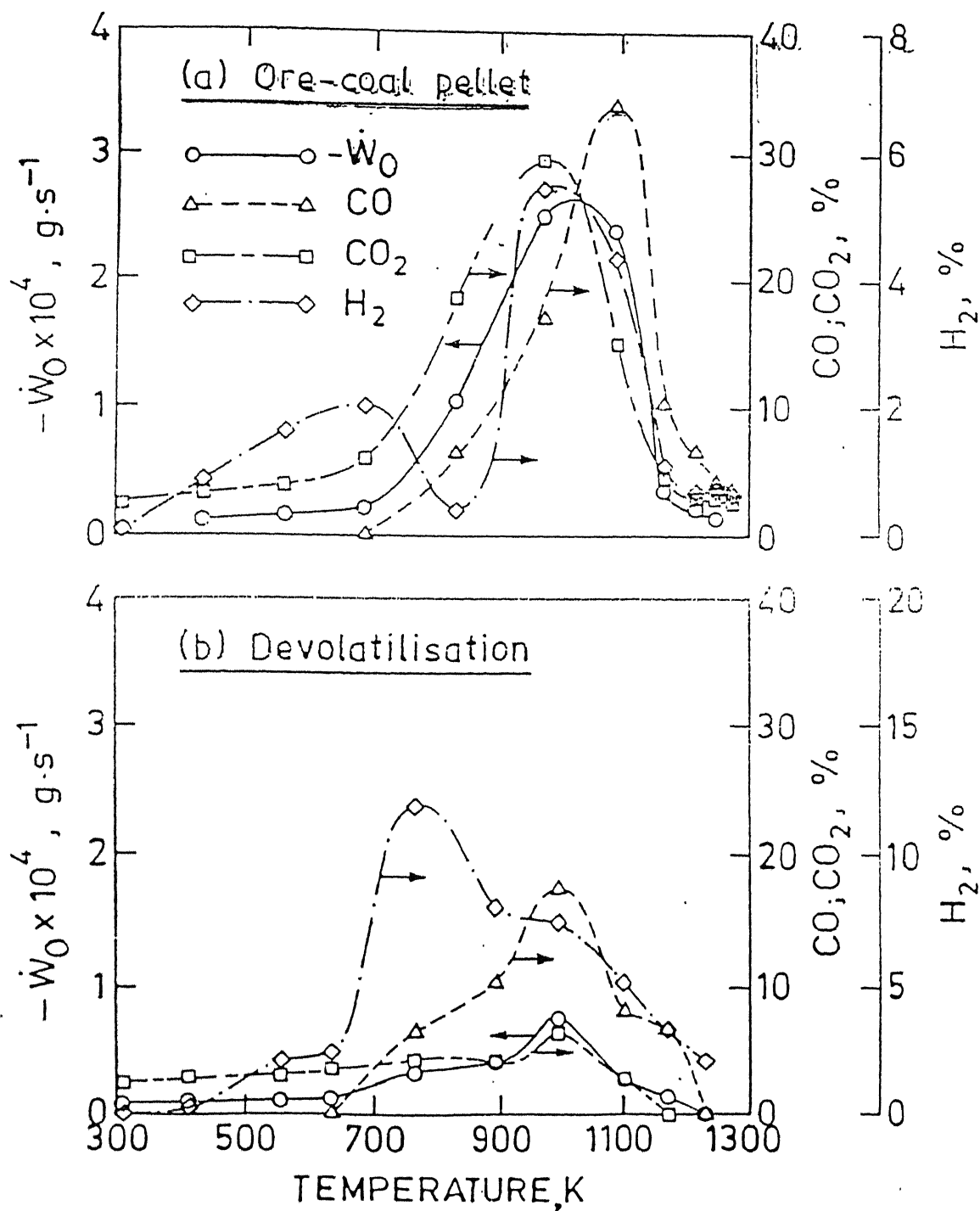
Figure 2.8: Variation of exit gas composition and $-\dot{W}_o$ with temperature in non-isothermal studies at low heating rate of low percentage Bachra coal .[35]

the above methods are not reliable. Investigators over the years have adopted different procedure for the determination of degree of reduction for composite pellets, which are discussed in chapter 3.

Scanning electron microscopy(SEM) of partially reduced pellets revealed typical features such as growth of whiskers,sintering of iron layer,ridges of wustite. Whiskers are dominant for high degree of reduction(above 80pct.

Some recent studies on fundamentals of either ore-coal mixtures or composite pellets are worth mentioning. Prakash and Ray [37] employed iron ore and non-coking coal mixture of either -10 +6 or -6 +3 mm size. They did not separate carbon and oxygen loss,and employed overall fractional conversion parameter for analysis of data. Both isothermal and non-isothermal studies were carried out. Degree of reduction was determined by method of Gonzales and Jeffes [38]. For isothermal experiments,Ginstling-Brounstein model was found to fit data. The Ginstling-Brounstein equation is given below.

$$\left[1 - \frac{2}{3}F - (1-F)^{2/3}\right] = \frac{kt}{R_o^2} \tag{2.11}$$

where F is the fraction reacted at time t, R_o is the initial radius of the oxide pellet. However, data were analyzed with a different mathematical procedure for non-isothermal experiments.

Huang and Lu [33] employed mixtures of ore-coal fines in cylindrical steel crucible,118mm i.d. and 150mm height,and introduced into a muffle furnace kept at 1473K. Thermocouples were installed in different locations of the mixtures,and temperature-time data were obtained. Considerable temperature gradient existed in the sample,specially in the beginning. Even after 60 minutes,the difference of temperature between the innermost and outermost location was as large as 300K. Also less carbon reacted at the interior than at surface. Based on temperature profiles and mathematical analysis,it was concluded that heat transfer was rate limiting.

Nascimento et al [39] carried out microstructural studies by SEM etc. of composite pellets reduced at temperatures between 1223-1423K. They employed mixtures of fines of iron ore and wood char(with 20pct.VM). Portland cement with water was the binder. They observed transgranular cracks during hematite $\rightarrow$ magnetite reduction stage. Wustite was porous presumably due to gas

evolution. Metallic iron was also porous. Whiskers were observed as well.

In industrial practices, the pellets are likely to be reduced at high temperature in reactive gas atmosphere. Very little published information is available in literature. Recently Ghosh [40] et al carried out some preliminary experimental measurements of reduction of some ore-coal cold-bonded composite pellets at 1256K in some gases and gas mixtures. It was found that the gaseous atmosphere had significant influence on reduction behaviour.

Chapter 3

EXPERIMENTAL PROCEDURE AND APPARATUS

3.1 Trials with pellet making

It was earlier decided to make pellets of cylindrical shape with iron ore fines and graphite powder,and small amount of water without the use of any binding material. As our purpose of study was fundamental in nature,use of any extraneous organic binder would make the system complex. Three alternatives were tried out for making pellets which would not crumble during handling or after reduction,since these would lead to erroneous results.

In the first trial iron ore fines were mixed with graphite and a little bit of water and were subjected to a compaction pressure of 7.7 Kg/mm^2 and 10.8 Kg/mm^2 for one minute.Then the pellets were taken out and oven dried at 100°C for 2-3hrs. It was found that the pellets crumbled after oven drying.

In the second trial it was decided to use a little bit more water and the pellets were subjected to the same compaction pressure as mentioned above and left for 2 minutes in the machine. Pellets were then taken out and oven dried for 5 hrs. in stages at temperatures of 50°C,100°C and 150°C respectively.But the pellets crumbled while handling.

In the third trial 2 % bentonite was employed as binder along with water, and the same procedure as mentioned for second trial was repeated. It was found that still the pellets did not

Table 3.1: Size analysis of blue dust and graphite

SL. No.	Mesh size	Blue dust(%)	Graphite(%)
1	-100 +200	72.49	52.55
2	-200 +230	25.33	38.68
3	-230	2.16	8.75

achieve the desired strength. It was also desirable not to use too high pressure to make the pellets because the product gases coming out after reduction may cause crumbling of the pellet thereby destroying its integrity. So it was decided to work with mixture of iron ore fines and graphite in a stainless steel crucible and compact it in a pellet making unit as shown in Fig.3.1.The crucibles containing mixture of iron ore fines and graphite was first kept on the platform, the mandrel was then placed just above the crucible and supported by hand. The impact load(0.45Kg) was then unscrewed from a height of nearly 13cm and allowed to fall on the mandrel.

3.2   Raw material preparation and characterization

3.2.1   Size

Our aim was to carry out experiments with raw materials(blue dust and graphite) of -100 mesh size. For blue dust no grinding was necessary as it was very fine. Sieve analysis was done with sieves of BSS mesh size 100, 200 and 240 with opening sizes of $152\mu m, 76\mu m$ and $66\mu m$ respectively.The results are presented in Table 3.1. Graphite was pulverized in a pulverizer (FRITSCH make-00502). After pulverizing,sieve analysis was carried out with sieve of the same mesh sizes as mentioned before,the results of which are presented in Table 3.1.

3.2.2   Chemical characteristics

Dutta [21] used the same blue dust as in this study. He carried out analysis of the blue dust using two methods,viz. chemical analysis and hydrogen reduction. The latter gave data on removable oxygen associated with Fe_2O_3.The results of his analysis is presented in Table 3.2. For
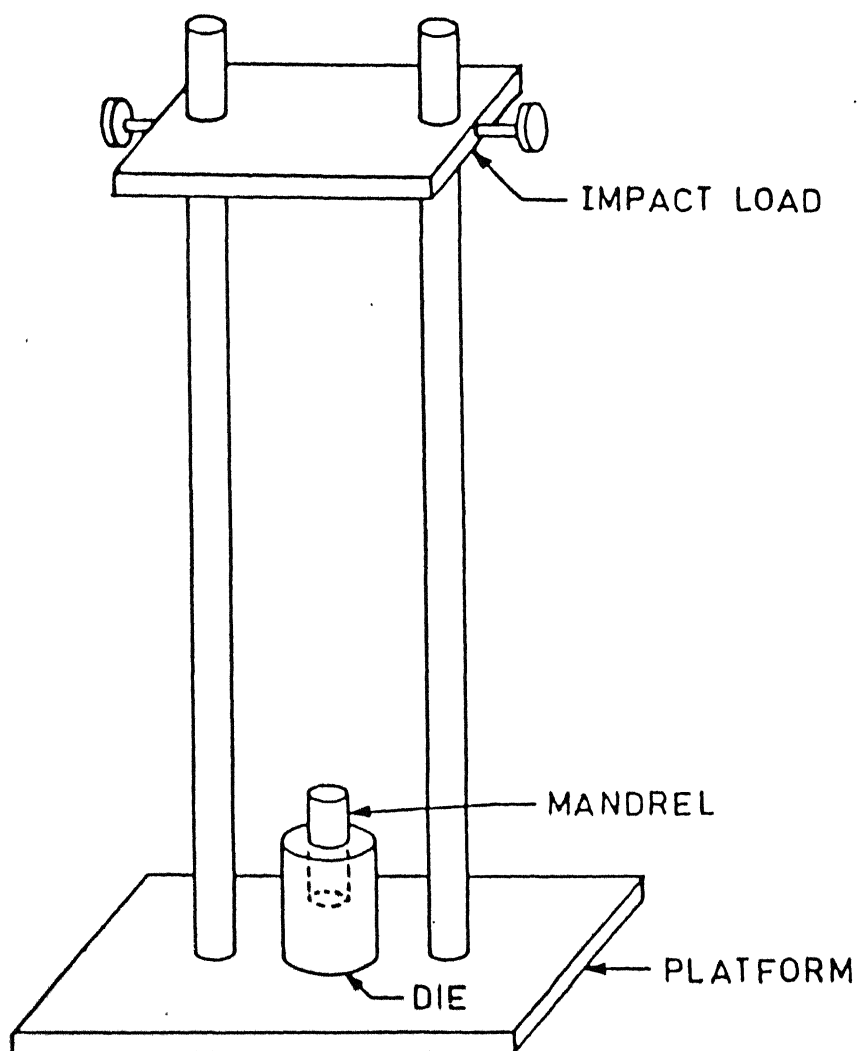
Figure 3.1: Schematic representation of pellet making unit

Table 3.2: Analysis of Blue dust

Total Fe (%)		Total Removable Oxygen (%)		Fe₂O₃ (pct) (By Chem Analysis)	(By H₂ Red)		Moisture (%)		LOI (%)	
	Av*		Av*			Av*		Av*		Av*
66.7		28.6					0.07		0.70	
	66.5		28.8	95.1	95.7	95.4		0.07		0.72
66.3		29.0					0.07		0.73	

Fe^{2+} = negligible, SiO_2 = 1.6 pct, Al_2O_3 = 1.8 pct

Av* = Average,   LOI = Loss on ignition

graphite, proximate analysis was carried out to determine the volatile matter and the ash content following the standard procedure.

the standard procedure. It was found that the VM was 3.3%.

Since the solid reductant should be carbon only for the present study, it was intended to reduce the volatile matter content. To do that an alumina crucible(i.d.-5.5cm,height-12.5cm) was used with a cover of graphite. The crucible with 25gm of graphite powder was inserted in the muffle furnace at a temperature of 600°C and kept for 45 minutes. Thereafter the crucible was kept for another one hour in the furnace and the temperature was slowly raised from 600°C to 800°C .Then it was taken out and cooled and further measurements were carried out. The data obtained after this operation is as follows:

VM - nil

Moisture - nil

Ash - 0.02%

Fixed carbon- 99.98%

3.2.3   Method of mixing and handling

Due to difference in densities of iron ore fines and graphite, proper care was taken during mixing and handling of the mixture because of the possibility of segregation.In order to avoid this the following procedure was adopted.

All the constituents were first of all mixed in a bottle for 20 twenty minutes by hand rolling. Shaking was avoided in order to prevent segregation . The mixture was then transferred to a pulverizer(FRITSCH make-00502) without balls and kept for 5 minutes.The mixture was then transferred to the bottle and again hand rolled for 10 minutes and carefully kept in the desicator. Before use it was again hand rolled for 10 minutes. To avoid segregation during handling the bottle containing the mixture was taken out and kept very carefully from the desicator without giving any jerk.

3.3   Apparatus for reduction experiments

3.3.1   Furnace

The reduction experiments were carried out in a horizontal tube furnace, as shown in Fig.3.2. At one end the furnace head was connected with the inlet gas tube i.e,the tube through which the gases such as Ar, H_2, CO_2 are introduced into the furnace. At the other end through which the crucibles were introduced,the furnace head was connected with a bubbler to prevent any air entering the furnace. Temperature of the hot zone was measured by a chromel-alumel thermocouple. Fig.3.3. shows the temperature profile along the axis of the furnace. The mullite tube had i.d.45mm,o.d. of 50mm and a length of 570mm. The furnace was 510mm long with outside diameter of 280mm. Although chromel-alumel thermocouple had been employed for temperature profiling, Pt-Pt/10%Rh controller was only available in working condition. Hence for subsequent temperature measurement and control Pt-Pt/10%Rh thermocouple was employed. The controller was Indoterm make-401. It was a power proportionating controller with a control sensitivity of plus-minus 2°C. The temperature measurement was done by a digital millivoltmeter(Agronic-152) with a precision of plus-minus 0.01mv.

INLET GAS →

Bubbler

Horizontal tube furnace

Cold junction

Millivoltmeter

INDOTHERM-401

Controller

Fig 3.2 : Horizontal Tube Furnace

Distance from the midpoint of the furnace (cm) -->
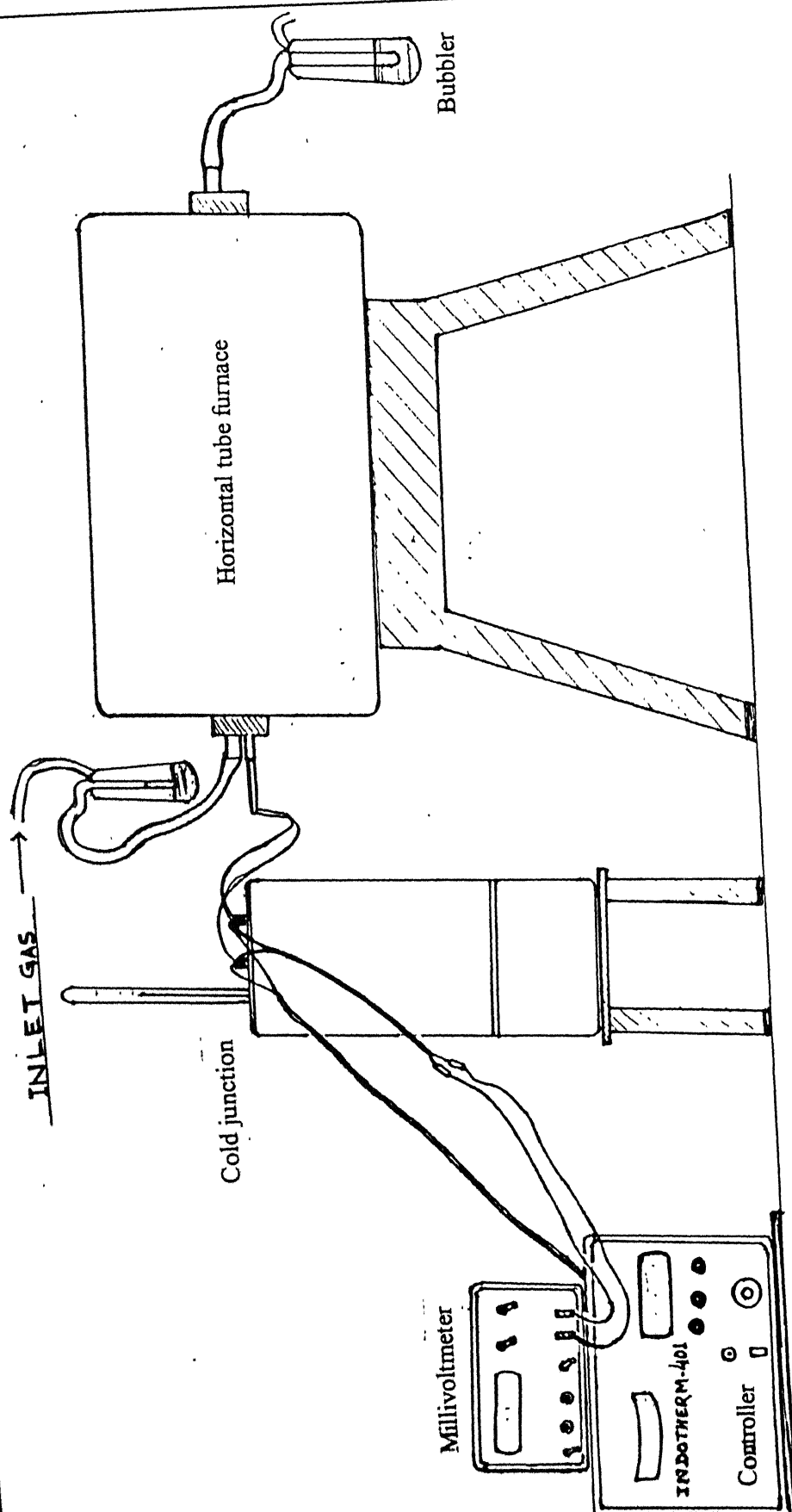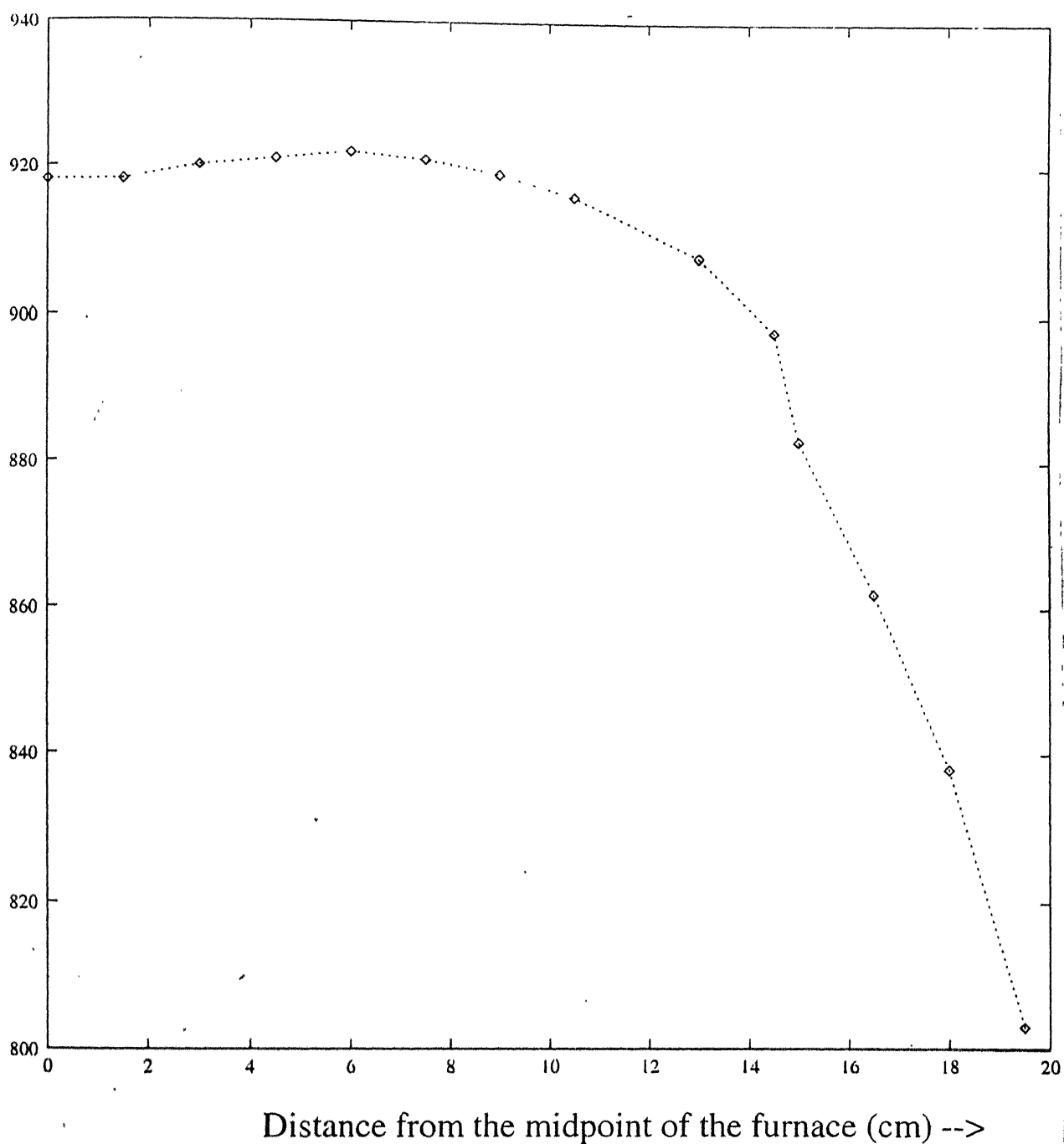
Figure 3.3: Temperature profile along the axis of the furnace

3.3.2 Gas train

The gas train is shown in Fig.3.4. It consists of cylinders of Ar,H_2 and CO_2 which were connected to the flowmeters as per requirements of the experiments. The flowmeters were calibrated for all the three gases with the help of wet test meter. The calibrated readings of the flowmeters being used for all the gases are presented as linear best fit equation below and graphically represented in Fig.3.5 and Fig.3.6.

Flowmeter 1

$$Q_{Ar} = 0.146 + 0.13\Delta h \tag{3.1}$$

$$Q_{CO_2} = -0.36 + 0.226\Delta h \tag{3.2}$$

$$Q_{H_2} = -1.01 + 0.39\Delta h \tag{3.3}$$

Flowmeter 2

$$Q_{Ar} = 0.18 + 0.09\Delta h \tag{3.4}$$

$$Q_{CO_2} = 0.13 + 0.127\Delta h \tag{3.5}$$

$$Q_{H_2} = 0.01 + 0.23\Delta h \tag{3.6}$$

where Q = Flowrate (Cm^3/sec) at STP

Δh = Height difference (Cm)

Argon was passed through a furnace containing BTS catalyst (manufactured by BASF,Germany) for removal of trace oxygen. This catalyst has fine copper particles dispersed on a porous oxide pellet.Anhydrous $Cacl_2$ tube was meant for removal of moisture. The operating temperature of BTS catalyst furnace was 180ºC. The BTS catalyst was regenerated time to time by treating it with hydrogen.

1.	GAS CYLINDER
2.	NEEDLE VALVE
3.	BUBBLER
4.	CAPILLARY FLOWMETER
5.	MIXING CHAMBER
6.	BTS CATALYST FURNACE
7.	TWO WAY STOP COCK
8.	ANHYDROUS $CaCl_2$ COLUMN
9.	HORIZONTAL FURNACE
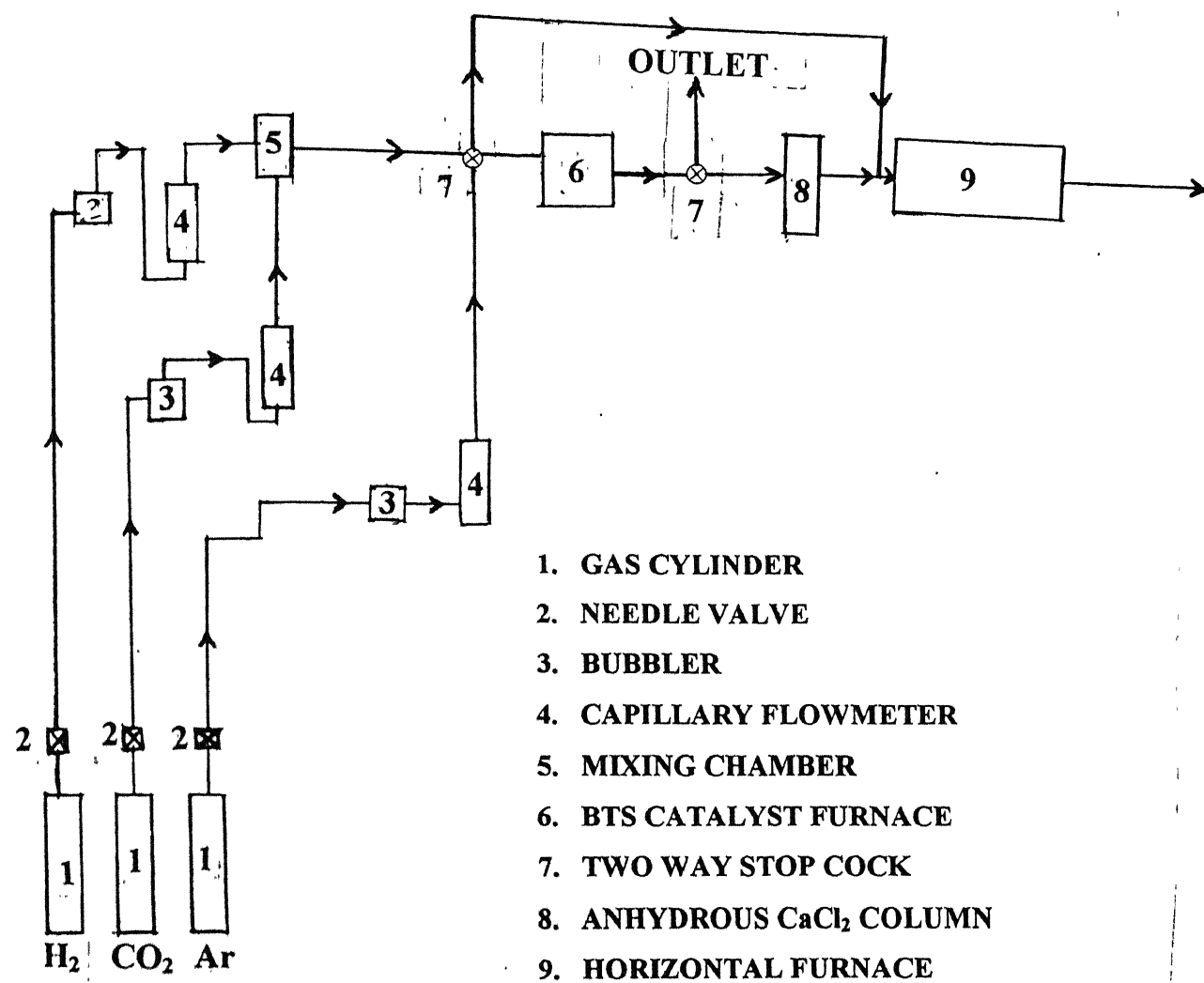
Figure 3.4: Schematic representation of the gas train
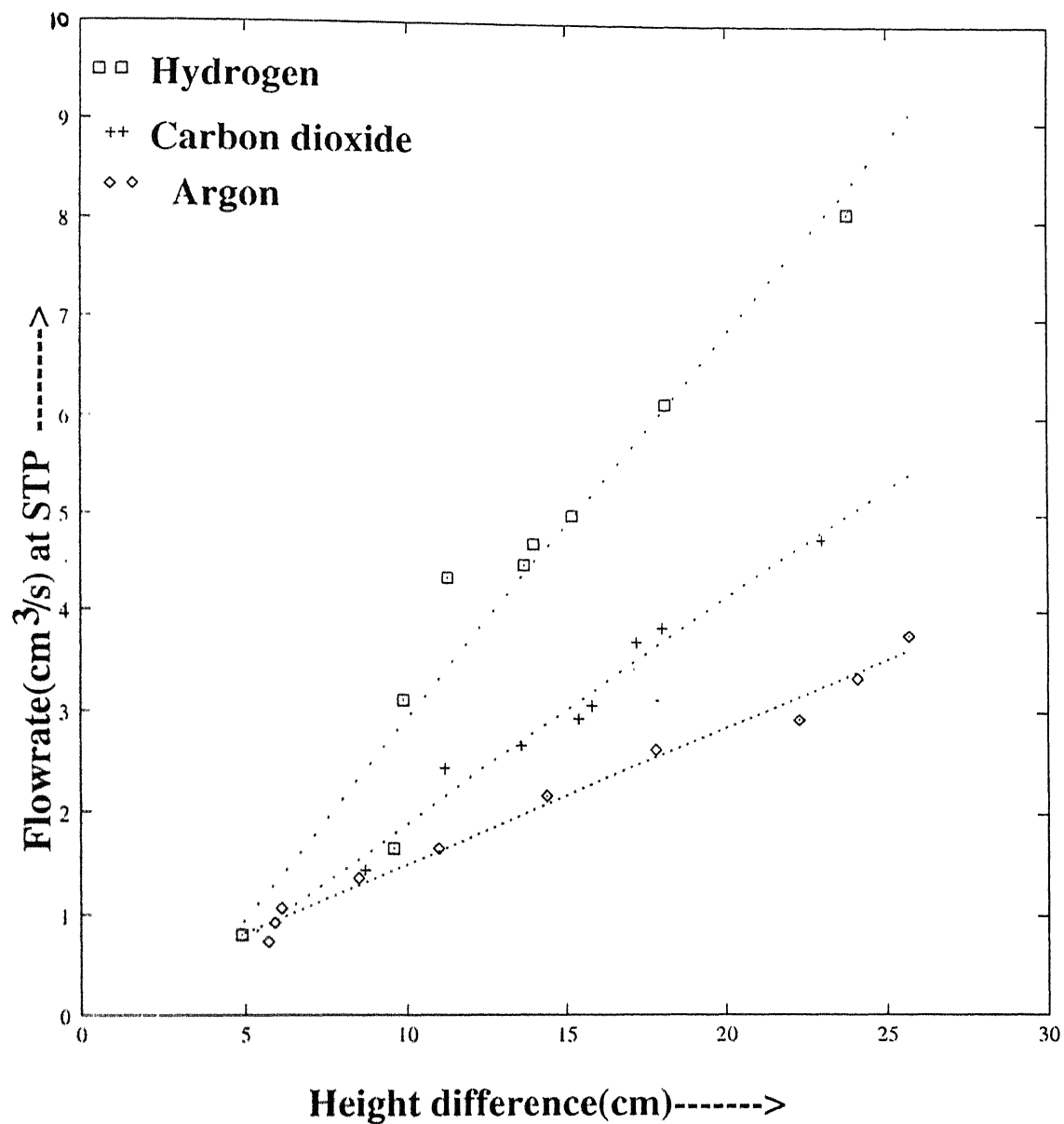
Figure 3.5: Graphical representation of calibrated readings in flowmeter 1 for the three gases used.
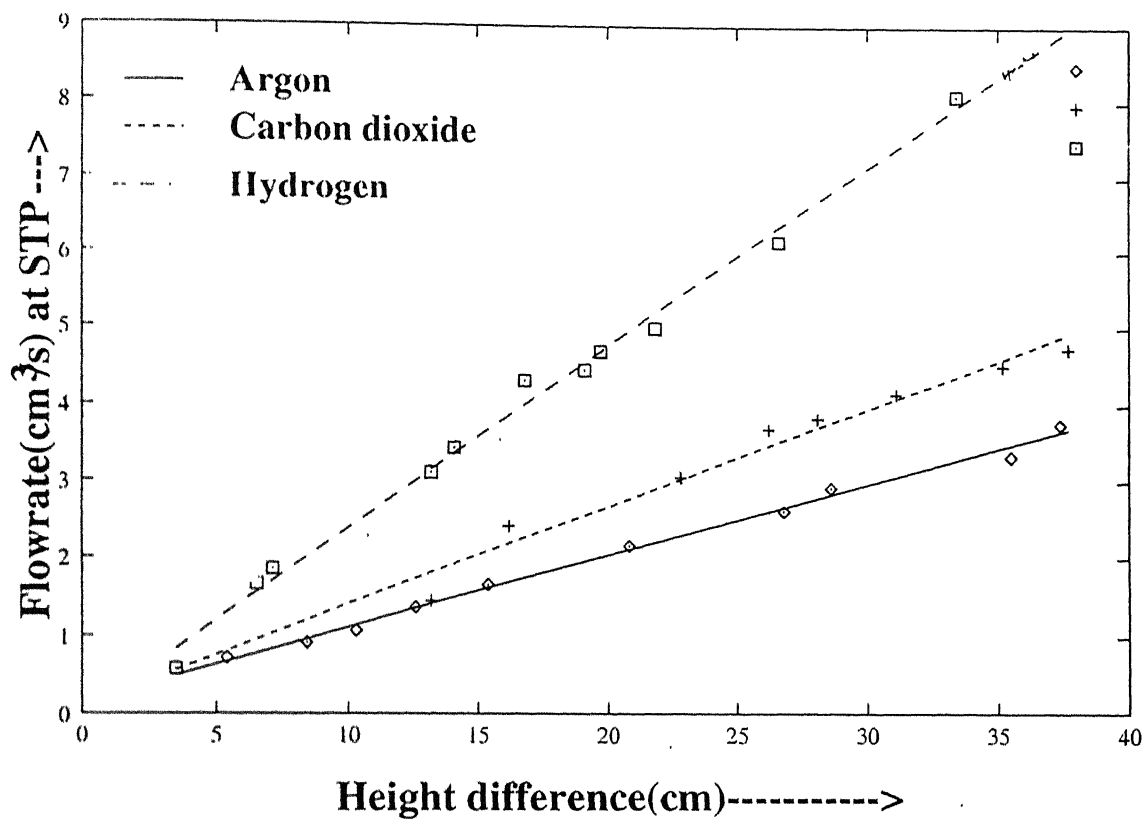
Figure 3.6: Graphical representation of calibrated readings in flowmeter 2 for the three gases used.

3.4 Procedure for reduction experiments

3.4.1 Reduction in Argon or mixture of CO_2 and H_2

The furnace was first allowed to attain the set temperature. Argon was then passed through the furnace for nearly 5 minutes with a flow rate of approximately $5cm^3/s$ before inserting the sample. The weighed samples were then introduced into the furnace by opening the furnace head, the argon flow being continued. The refractory boat with 2 stainless steel crucibles, one size each (i.d.-1.1cm,height-1cm and 0.6cm respectively), containing mixture of iron ore fines and graphite powder was initially kept in the cold zone of the furnace for nearly one minute. The furnace head was closed and the flow rate of argon was lowered to the desired flow rate at which it was intended to study reduction behaviour in argon.

In case of CO_2 and H_2 mixture argon flow was stopped and the flow rate of CO_2 and H_2 gaseous mixture adjusted as per requirement. The boat was then slowly pushed to the hot zone of the furnace,the experiments carried out for specified time in the desired gas . Then the gas flow rate was stopped if it was CO_2 and H_2 mixture. The boat was then taken out into the cold zone of the furnace and kept their under argon flow for 2-3 minutes.

The furnace head was then removed and the boat taken out on an asbestos sheet and covered with a cover made up of almunium (slightly bigger in size than that of the boat) with minimum time gap so that there is no re-oxidation of reduced iron. After the crucibles had sufficiently cooled down they were placed in a desicator for some time and then weighed. All weighings were done in an electronic analytical balance (Sartorius).

3.4.2 Procedure for determination of degree of reduction

For reduction of iron oxides by carbon,a major difficulty with experiments is that the extent of reduction cannot be found out directly from the weight loss of the sample ,since this is made up of both oxygen and carbon losses. Apart from this there is a weight loss due to volatile matter and moisture if present. Since only weight loss of the sample is not sufficient, some additional measurements are required for estimating the degree of reduction(F) which is defined as follows

$$F = \frac{wt\ of\ oxygen\ removed\ from\ iron\ oxide}{total\ wt\ of\ oxygen\ present\ in\ iron\ oxide} \qquad (3.7)$$

Investigators adopted different procedures for determination of F for composite pellets. Some chemically analyzed the reduced mass, and used this information either alone or with overall weight loss data in order to estimate F. Amongst them the procedure adopted by Bryk and Lu [43] was the most general,and is applicable to all types of carbonaceous reductant with or without binder. Gonzales and Jeffes[38] have proposed a method of estimation of the chemical composition of partially reduced iron ore samples. The method of determining the composition of the reduced samples requires an accurate initial chemical analysis of the material including gangue and loss of ignition. This technique is however not applicable for composite pellets due to presence of carbonaceous reductant in the pellet.

Dutta and Ghosh [41] found earlier procedures to be unsatisfactory and carried out trails to develop a satisfactory procedure for determining F. In this procedure, further reduction of reduced composite pellets was carried out in a thermogravimetric set up in flowing hydrogen. The degree of reduction was calculated by the following equation.

$$F = \frac{W_o^i - \Delta W_o^H}{W_o^i} \qquad (3.8)$$

where W_o^i is the total weight of oxygen present in the iron oxide and ΔW_o^H is the total weight loss during hydrogen reduction.

The above procedure was examined for two possible sources of error which are as follows:
(i) loss of carbon due to reaction of residual carbon with residual oxygen in pellet during hydrogen treatment of the partially reduced pellet.
(ii) loss of carbon due to reaction

$$C(s) + 2H_2(g) = CH_4(g) \qquad (3.9)$$

Considering the above factor they gave trails in order to determine how serious these sources of errors would be. After trails it was found that the error from these sources were insignificant and pct. error may be at the most 2% at 1023K for one hour at flow rate of 5cm^3/s at STP.Dutta and

others subsequently employed this procedure for determination of F and it has been adopted here.

The partially reduced mixture of iron ore and graphite was crushed. The crushed sample was then taken in the same crucible to which it belonged. The procedure consist of cleaning the crucible with dil. *Hcl* before taking fresh sample. As already stated earlier ,the hot crucibles were sealed by a cover from the atmospheric air immediately upon taking out from the furnace. The crucible along with the sample was then weighed.

The furnace chamber was then flushed with argon at 5cm^3/s for nearly 5 minutes,the furnace being at a temperature of 750°C. The refractory boat containing the crucibles with weighed amounts of partially reduced samples, was then inserted following the steps described for reduction experiments. The argon flow then stopped and hydrogen was passed at 3.32cm^3/s for one hour. After one hour the samples were taken out and stored as described previously, while taking out the boat hydrogen flow was stopped and argon flow started at 5cm^3/s. The samples were cooled as described previously. After cooling the samples were weighed and the amount of residual oxygen calculated.

Chapter 4

RESULTS AND DISCUSSION

4.1 Results

The experiments conducted had the following variables:

i)temperature(1150K,1250K,1300K)

ii)Fe_2O_3/C mass ratio (3:1 and 4.5:1)

iii)sample size (big crucible i.d=1.1cm and height=1cm,small crucible i.d=1.1cm and height=0.6cm)

iv)gas composition (H_2 :CO_2=3:1, H_2:CO_2=1.5:1, argon).

Therefore the there were 36(3*2*2*3) experimental conditions all together. In each condition measurements were made at time durations of the sample in the hot zone,viz. 600,1200,1800,2400 and 3000 seconds. This makes total of 180 set of data and some of which were repeated also. Total gas flow rates were kept constant at 4cm^3/s (STP) for all experiments.

The experimental codes given in Appendix1,Appendix2 and Appendix3 consist of eight digits. The first digit in all the codes is represented by the letter g, which stands for the reductant graphite. The explanation for the remaining seven digits is given below.

2nd and 3rd digits represent the Fe_2O_3/C mass ratio,that is 30 and 45 for ratios 3,4.5 respectively.

4th and 5th digits represent the temperature,that is 11,12,13 for 1150,1250 and 1300K respectively.

6th and 7th digits represent the gas composition,that is h1,h2,ar for H_2:CO_2=3,H_2:CO_2=1.5 and argon.

8th digit represents the size of the sample,that is s for small and b for big.

For example, the code g3011h1b means experiments with graphite as reductant, Fe_2O_3/C mass ratio=3,at a temperature of 1150K,with $H_2:CO_2$ mass ratio =3.0 in a big crucible.

The degree of reduction was calculated by the following equation

$$F = \frac{Wio - \Delta W_o^H}{Wio} \tag{4.1}$$

where Wio is the initial weight of removable oxygen in the sample and ΔW_o^H is the total weight loss during hydrogen reduction.

To illustrate the procedure of calculation, one sample calculation with experimental code g3012arb with reduction time of 600 seconds is shown below.

The experimental data for the above mentioned code and time are as follows:

(i)mass ratio = 3.0

(ii)weight of the sample(Ws) was 0.9963gm

(iii)weight after reduction was 0.955gm

(iv)weight before hydrogen reduction was 0.939gm

(v)weight after hydrogen reduction was 0.8198gm

Amount of blue dust = K $\times$ 0.9963gm

where,K is equal to 0.7586 for mass ratio 3.0 and 0.8248 for mass ratio 4.5

Therefore, amount of blue dust = 0.7557gm

Amount of Fe_2O_3 =0.7557gm $\times$ 0.954= 0.7209gm(since blue dust contains 95.4% Fe_2O_3)

So,Wio =0.7209gm $\times$ 0.3 = 0.2162gm.

Therefore,

$$F = \frac{0.2162 - (0.939 - 0.8198)}{0.2162} \times \frac{0.955}{0.939} = 0.439 \tag{4.2}$$

Appendix1, 2 and 3 present the experimental data and calculated values of F under different experimental conditions.

F Vs. Time data for each experimental condition was fitted with a polynomial of the following form

$$F = a + bt + ct^2 + dt^3 + et^4 \tag{4.3}$$

where t is time in seconds. The coefficients were evaluated by regression analysis using standard GNUPLOT. The values of the coefficients have been reported in Appendix1,2 and 3. Fig.4.2 to Fig.4.13 present the fitted curves along with the experimental data points.

4.2 Discussions of results

4.2.1 General features for experiments in argon

In argon the exit gas would consist of Ar + CO + CO_2, the latter resulting from reaction of Fe_2O_3 with carbon. Argon is simply an inert flushing gas. Here the reaction mechanism and kinetics are relatively simple. One complication comes from catalysis of gasification reaction i.e

$$C(s) + CO_2(g) = 2CO(g) \tag{4.4}$$

by reduced metallic iron

As stated in chapter 2 that reduction of Fe_2O_3 fines is stage-wise,viz. $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow Fe_xO \rightarrow Fe$. For stoichiometric FeO metallic iron starts forming above a degree of reduction of 1/3 (i.e. approx. 0.33). However Wustite is non-stoichiometric, hence metallic iron is expected to form somewhere earlier than this value of F. As stated in chapter 2, significant catalytic enhancement by metallic iron has been reported in reduction of Fe_2O_3 by graphite.

If the reaction is

$$Fe_2O_3(s) + 3C(s) = 3FeO(s) + 3CO(g) \qquad (4.5)$$
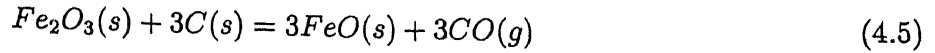
then the stoichiometric ratio of Fe_2O_3/C is 1:3 and mass ratio 4.44:1, therefore the sample with Fe_2O_3/C mass ratio of 4.5 is stoichiometric. On the other hand the sample with Fe_2O_3/C mass ratio 3 has excess carbon.

4.2.2   Thermodynamic considerations for H$_2$-CO$_2$ gas mixture

When a mixture of H$_2$ and CO$_2$ is introduced into a high temperature zone, it undergoes water-gas shift reaction .

$$CO_2(g) + H_2(g) = H_2O(g) + CO(g) \qquad (4.6)$$
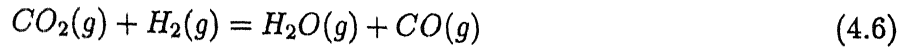
The equilibrium constant for this reaction is given by

$$K_{4.6} = \left[\frac{p_{H_2O} \times p_{CO}}{p_{CO_2} \times p_{H_2}} \right]_{eq} \qquad (4.7)$$

Assuming attainment of this equilibrium

$$\frac{p_{CO}}{p_{CO_2}} = \frac{K_{4.6} \times p_{H_2}}{p_{H_2O}} \qquad (4.8)$$

Again,$p_{CO} + p_{CO_2} + p_{H_2} + p_{H_2O} = p_T = 1$atm. For a given $\frac{p_{H_2}}{p_{H_2O}}$, therefore equilibrium $\frac{p_{CO}}{p_{CO_2}}$ ratio can be calculated from the above equations if $K_{4.6}$ is known.

Again, $\Delta G^o_{4.6} = -RT \ln K_{4.6}$

$\Delta G^o_{4.6}$ can be calculated from data on ΔG^o of formation of H$_2$O,CO$_2$ and CO.

$$\Delta G^o_{4.6} = \Delta G^o_f(CO) + \Delta G^o_f(H_2O) - \Delta G^o_f(CO_2) \qquad (4.9)$$

Based on the ΔG^o_f values from standard thermodynamic sources[45] values of $K_{4.6}$ and also the values of gas composition at 1150K,1250K, 1300K were calculated and have been presented in Table4.1.

It is fairly easy,thermodynamically speaking, to reduce Fe$_2$O$_3$ into Fe$_3$O$_4$ and Fe$_3$O$_4$ into FeO.

However it requires a high concentration of CO in CO/CO_2 to reduce Fe_xO into Fe. This is illustrated in Fig.4.1. Hence it is also important to calculate $\frac{p_{CO}}{p_{CO_2}}$ equilibrium value for the reaction

$$Fe_xO(s) + CO(g) = xFe(s) + CO_2(g) \tag{4.10}$$
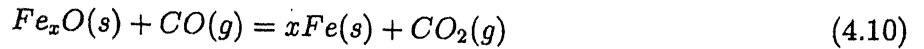
Based on free energy data from the same source these were calculated and are reported in Table 4.1

Table 4.1: Equilibrium p_{CO}/p_{CO_2} and K values for water gas shift reaction and equilibrium p_{CO}/p_{CO_2} values for $Fe_xO(s) + CO(g) = xFe(s) + CO_2(g)$ reaction at different temperatures

Temperature	Equilibrium (p_{co}/p_{co_2}) for Fe_xO + Fe	For water gas shift reaction		
		K	Gas ratio	Equilibrium (p_{co}/p_{co_2})
1150	1.706	1.18	$H_2{:}CO_2 = 3{:}1$	3.4
			$H_2{:}CO_2 = 1.5{:}1$	1.66
1250	2.06	1.44	$H_2{:}CO_2 = 3{:}1$	4.2
			$H_2{:}CO_2 = 1.5{:}1$	1.96
1300	2.234	1.76	$H_2{:}CO_2 = 3{:}1$	4.65
			$H_2{:}CO_2 = 1.5{:}1$	2.12

As it may be noted from Table 4.1 that, assuming equilibrium of water gas shift reaction, the gas mixture with H_2/CO_2 ratio of 3 is reducing to wustite. On the other hand, the gas mixture with H_2/CO_2 ratio of 1.5:1, is not reducing to wustite. Actually the experimental conditions were intended to be this way and that is why these two ratios were picked up and decided upon.

As noted in chapter 3, that some earlier investigations have established that the water-gas shift reaction attains equilibrium very fast at these temperatures. In order to allow this attainment of equilibrium, total gas flow rate was kept at a moderate value of $4cm^3/s$ based on observation [44].
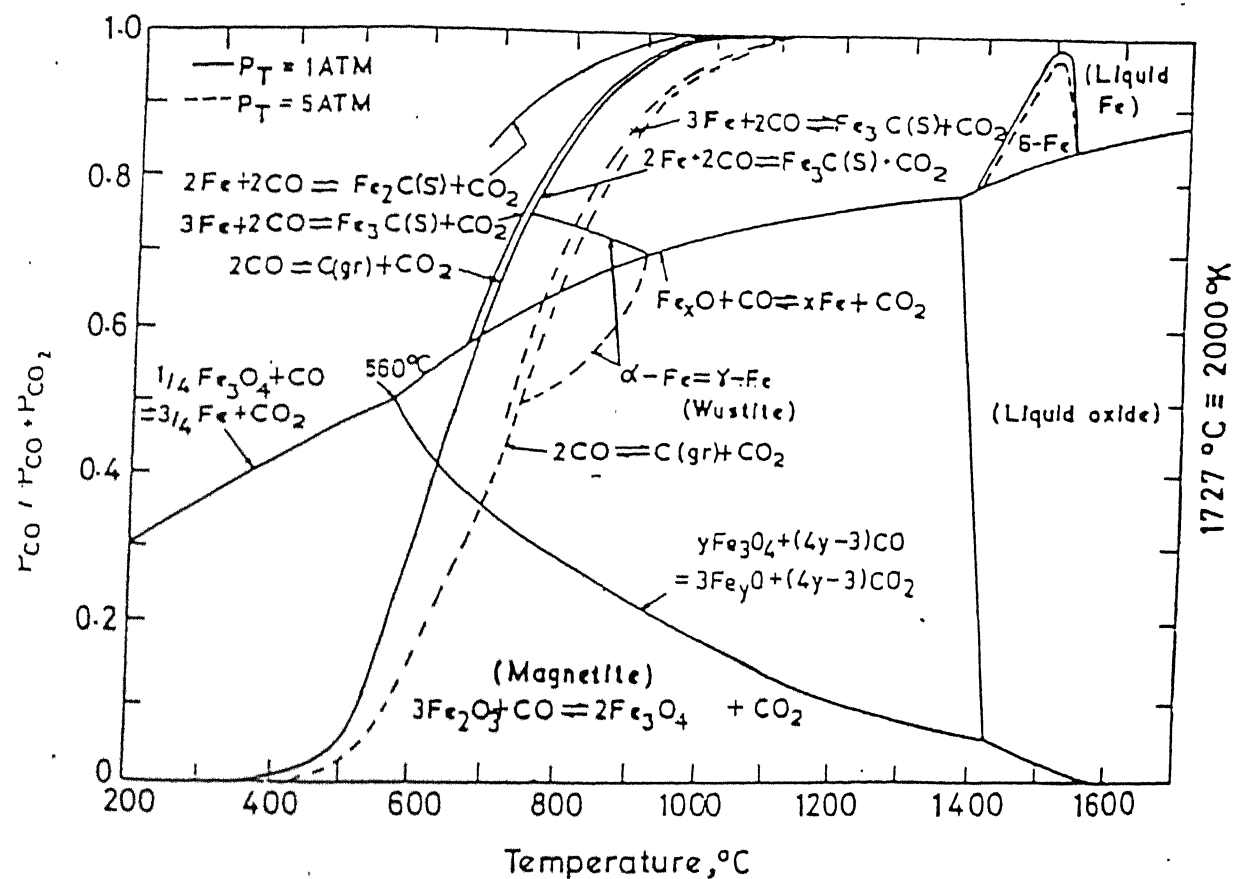
Figure 4.1: Equilibrium diagram for Fe-C-O system

4.2.3   General kinetic considerations for reduction behaviour in gas mixtures

In view of the water- gas shift reaction, the gas at high temperature would consist of H_2, CO_2, H_2O, CO, when a mixture of $H_2 + CO_2$ is introduced. For reduction of the oxide, therefore the following additional considerations have to be kept in mind in addition to those discussed in section 4.2.1 for reduction under argon atmosphere.

(i) Two additional gaseous species, viz.H_2 and H_2O are present. Hydrogen is expected to reduce iron oxide. Also in addition both H_2 and H_2O are known to influence the rate of gasification of carbon. Also H_2O oxidizes carbon. (ii) Concentration of CO and CO_2 in the gas will be considerably dictated by the water gas shift reaction, and this in turn will have their influence on gasification reaction and reduction reaction.

4.2.4   Variation of F with Time

Fig 4.2 to Fig4.13 shows variation of F with time. Each figure has data for the three gaseous atmospheres at a fixed condition otherwise. These have been arranged in this way in order to visualize influence of gaseous atmosphere on reduction behaviour. In order to discuss these results in a clear and concise fashion Table 4.2 has been prepared as a guide. From these, the following points may be noted.

(i)The degree of reduction is highest for almost all conditions for inlet gas mixture of H_2/CO_2 ratio of 3 in comparison to other gaseous environments. This is expected since, as per thermodynamic calculations presented in Table4.1,this gas mixture generates an atmosphere which is reducing to Fe_xO. The flowing gas is therefore expected to participate in reduction of iron oxides. Since H_2 is 5-10 faster reductant as compared to CO,this will contribute to enhancement of reduction further.

Table 4.2: Observations on F versus t behaviours

T (K)	Sample Size	Fe_2O_3/C Ratio	Fig no.	Observations (Relative magnitude of F)		
				$H_2/CO_2 = 3:1$	$H_2:CO_2 = 1.5:1$	Ar
1150	Big	3	4.2	Middle in the beginning but highest at the end	Lowest	Comparable to $H_2:CO_2=3:1$
	Big	4.5	4.3	Highest	Middle	Lowest towards the beginning but middle at the end
	Small	3	4.4	Highest	Lowest	Middle
	Small	4.5	4.5	Highest	Comparable to argon	Comparable to $H_2:CO_2=1.5:1$
1250	Big	3	4.6	Highest	Lowest till t=2600 sec. but middle at the end	Middle from t=800 to T=2600 sec., lowest at the end
	Big	4.5	4.7	Highest	Comparable to argon till t=2400 sec., but higher at the end	Comparable to $H_2:CO_2=1.5:1$ till T=2400sec.but lowest At the end
	Small	3	4.8	Highest	Lowest till t=2600 sec. but middle towards the end	Middle in most of the range
	Small	4.5	4.9	Lower in the beginning but highest after t=1200sec.	Lowest till t=2600 sec.	Highest in the beginning,middle from t=1200 to t=2600sec, lowest at the end
1300	Big	3	4.10	Highest	Middle at the beginning but comparable with $H_2:CO_2=3:1$ after t=1400sec.	Lowest in almost Entire range
	Big	4.5	4.11	Highest	Comparable with $H_2:CO_2=3:1$, little lower	Lowest
	Small	3	4.12	Highest	Middle in the beginning but comparable with $H_2:CO_2=3:1$ after t=1200 sec.	Lowest
	Small	4.5	4.13	Highest	Middle	Lowest

(ii)By and large in several cases, the degree of reduction is lowest with inlet gas of H_2/CO_2 ratio equal to 1.5. As Table4.1 shows that this gas mixture generates a p_{CO}/p_{CO_2} ratio, according to thermodynamic calculations, which is somewhat lower than that for the equilibrium of $Fe_xO \rightarrow$ Fe system. Therefore this will have a tendency to prevent reduction of Fe_xO into Fe. Stoichiometrically, two of every three atoms of Fe_2O_3 are removed in the FeO$\rightarrow$ Fe stage as follows:

$3Fe_2O_3 \rightarrow 2Fe_3O_4 \rightarrow 6FeO \rightarrow 6Fe$. That means out of every nine oxygen atoms in association with Fe_2O_3, six atoms get removed during FeO$\rightarrow$Fe stage. Hence if FeO$\rightarrow$ Fe reduction is prevented degree of reduction should not exceed approximately 0.33. However it is larger than that in all the cases, due to simultaneous reduction by graphite.

However there are some experimental conditions where the above generalizations do not hold good. Since the mechanism and kinetics of the reaction are complex, as stated in sec4.2.3, only brief remarks will be made on this as follows.

(i)At 1150K , F(degree of reduction) is highest for H_2+CO_2 gas mixture with H_2/CO_2 ratio of 3, this is as expected and discussed above. For Fe_2O_3/C ratio of 4.5 the quantity of carbon is stoichiometric as stated earlier in section4.2.1. Here the degree of reduction in argon was lower or comparable to that in gas mixture with H_2/CO_2 ratio of 1.5. However, with excess carbon in the sample, values of F in argon is far higher than those in gas mixture with H_2/CO_2 ratio of 1.5. This is expected. Other investigators (9,10,14) also found increase of degree of reduction with excess carbon in the sample as stated in the literature review.

(ii)At 1250K, the qualitative behaviour patterns are like 1150K, except that even for Fe_2O_3/C ratio of 4.5 and small sample size significant higher degree of reduction was observed(Fig.4.9) as compared to those in gas mixtures of H_2/CO_2 ratio of 1.5, except at time=3000seconds.

A possible explanation is that the CO_2 bearing external flowing gas enhanced rate of gasification of carbon significantly, thus generating more CO and hence higher degree of reduction. In the small sample, the influence of the flowing gas will be more significant as compared to the big sample because of higher surface to volume ratio in the former case.

(iii)At 1300K, again the degree of reduction is highest in gas mixture with H_2/CO_2 ratio of 3, as
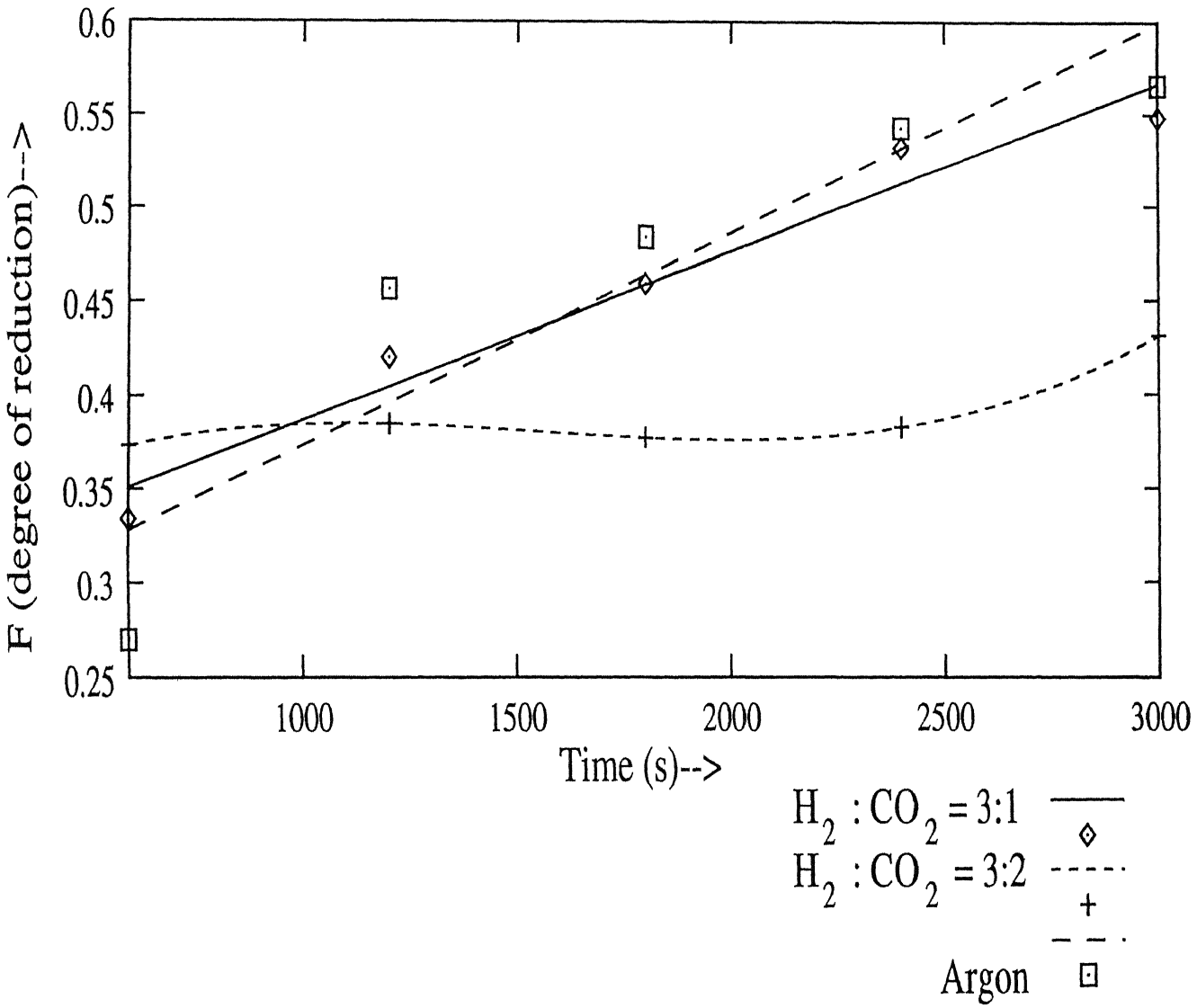
Figure 4.2: Variation of F with time for $Fe_2O_3/C = 3$ and big sample size at 1150 K
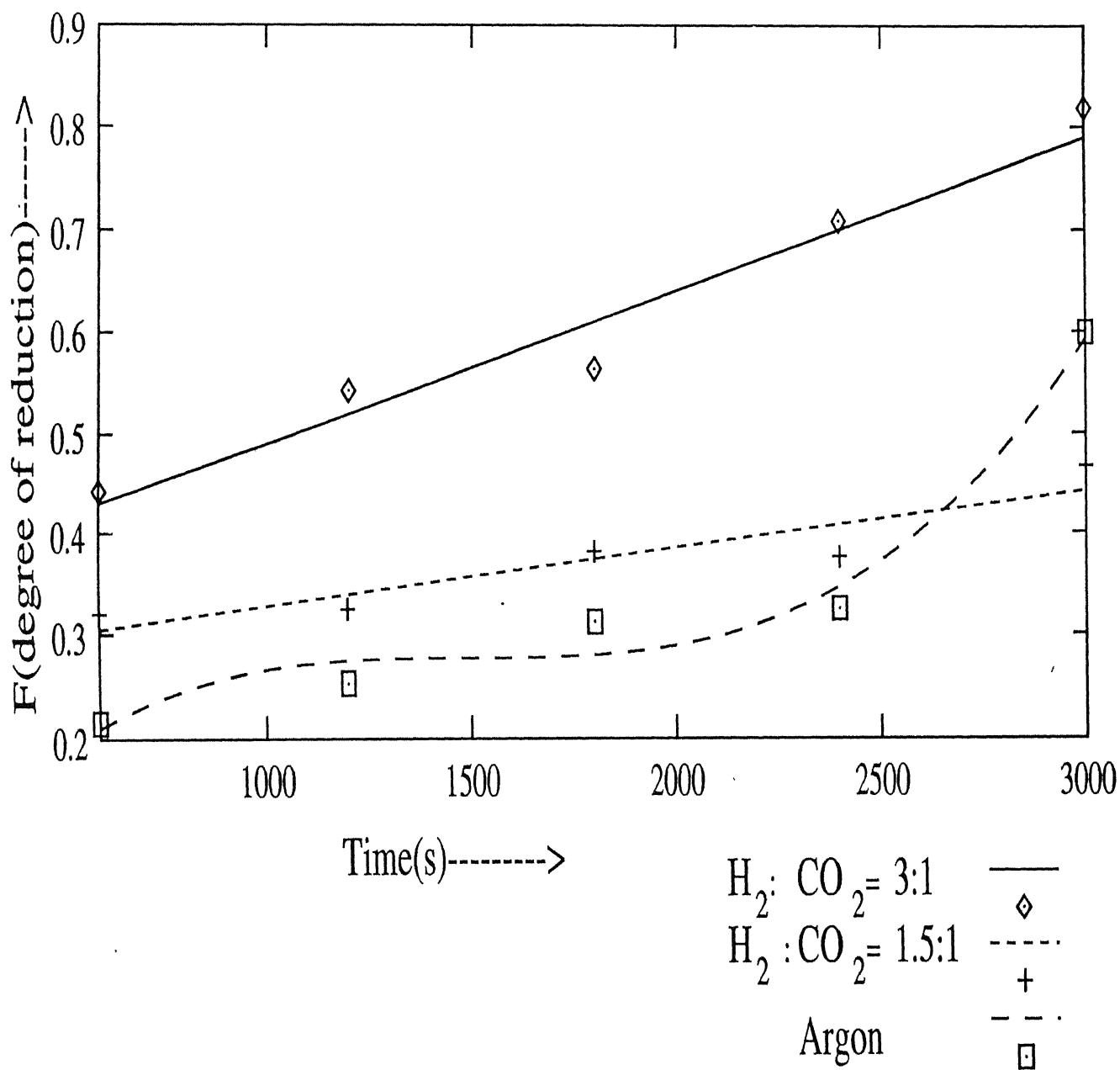
Figure 4.3: Variation of F with time for $Fe_2O_3/C = 4.5$ and big sample size at 1150K

Figure 4.4: Variation of F with time for $Fe_2O_3/C = 3$ and small sample size at 1150K

Figure 4.5: Variation of F with time for $Fe_2O_3/C = 4.5$ and small sample size at 1150K
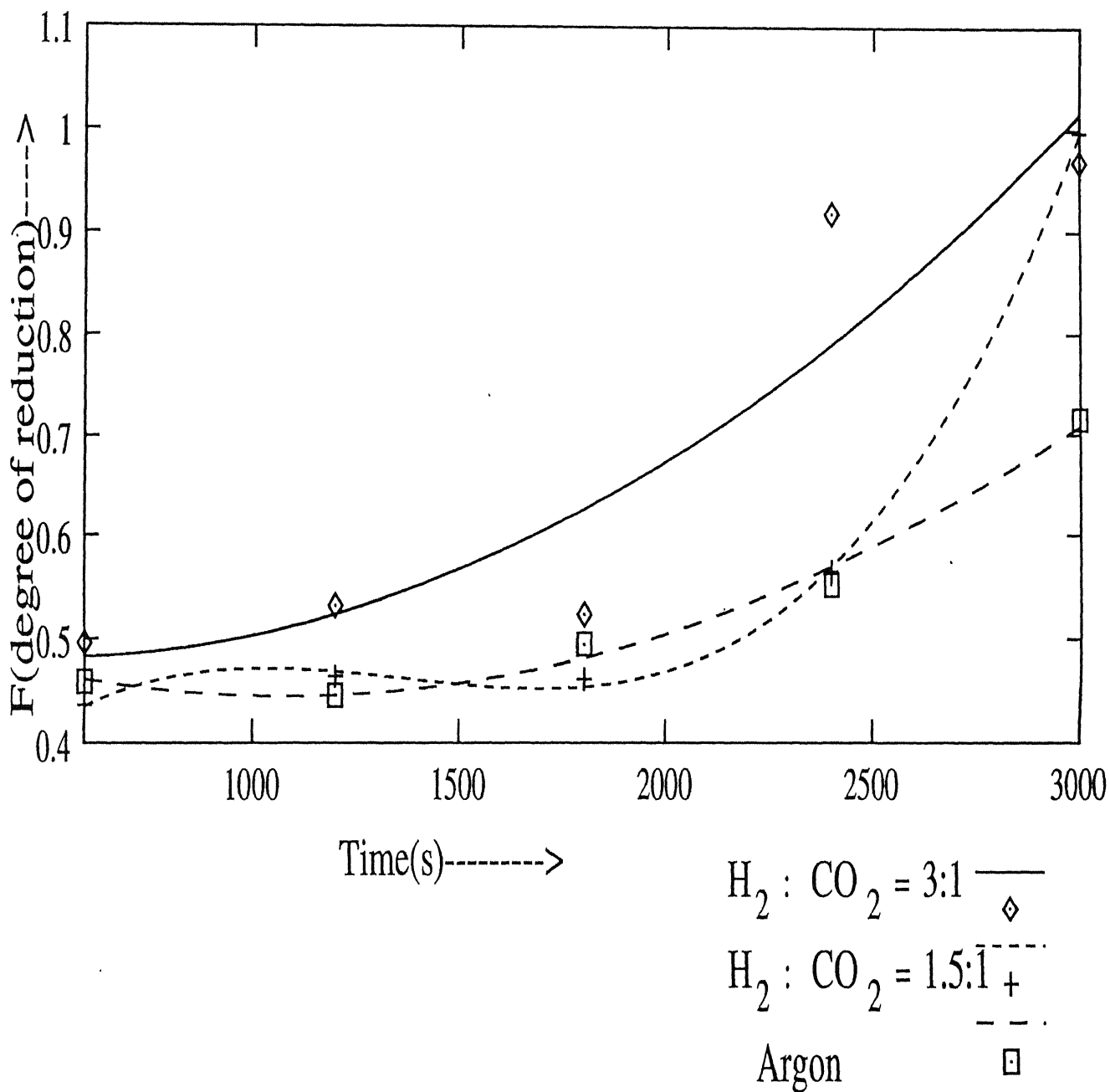
Figure 4.7: Variation of F with time for $Fe_2O_3/C = 4.5$ and big sample size at 1250K

Figure 4.8: Variation of F with time for $Fe_2O_3/C = 3$ and small sample size at 1250K

Figure 4.9: Variation of F with time for $Fe_2O_3/C = 4.5$ and small sample size at 1250K
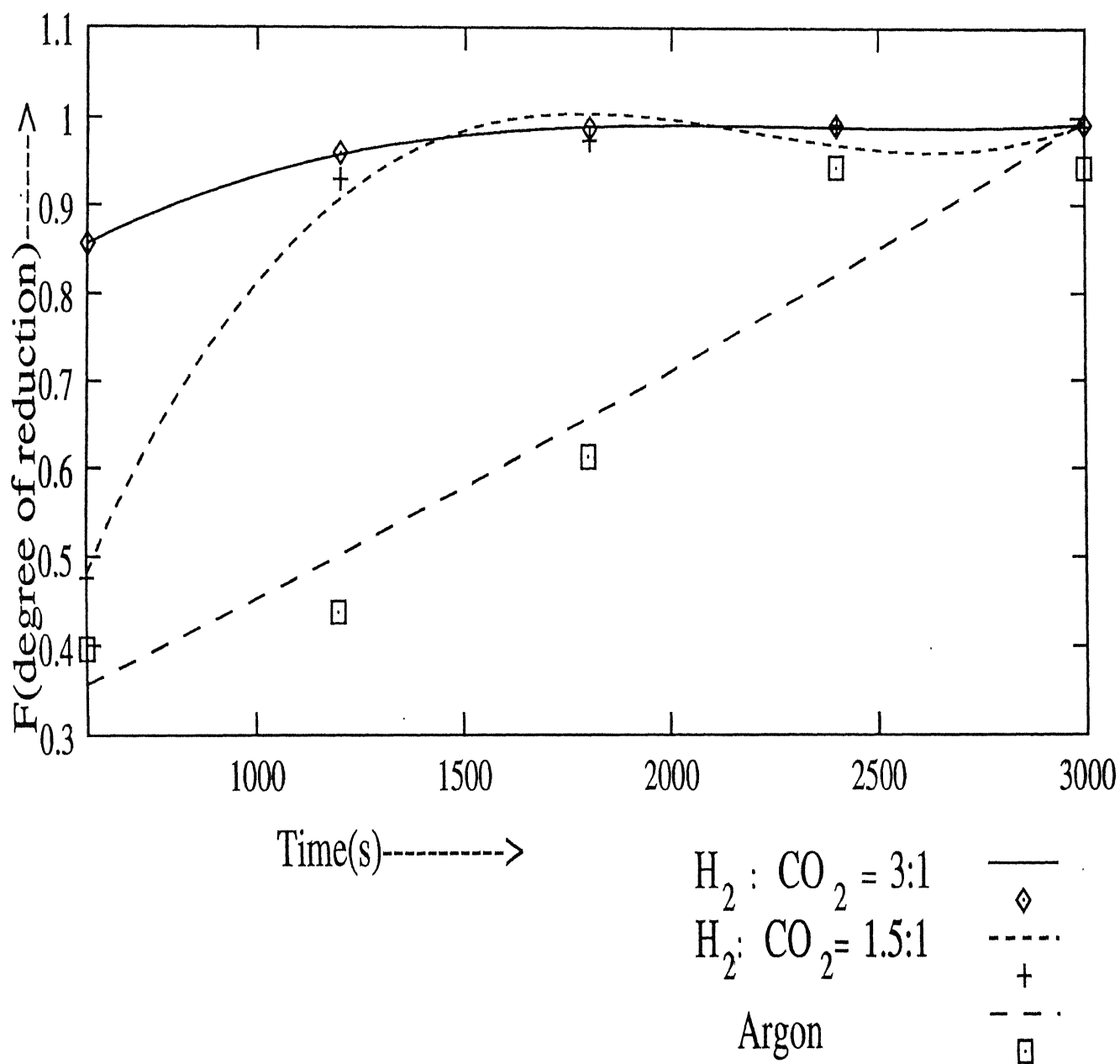
Figure 4.10: Variation of F with time for $Fe_2O_3/C = 3$ and big sample size at 1300K
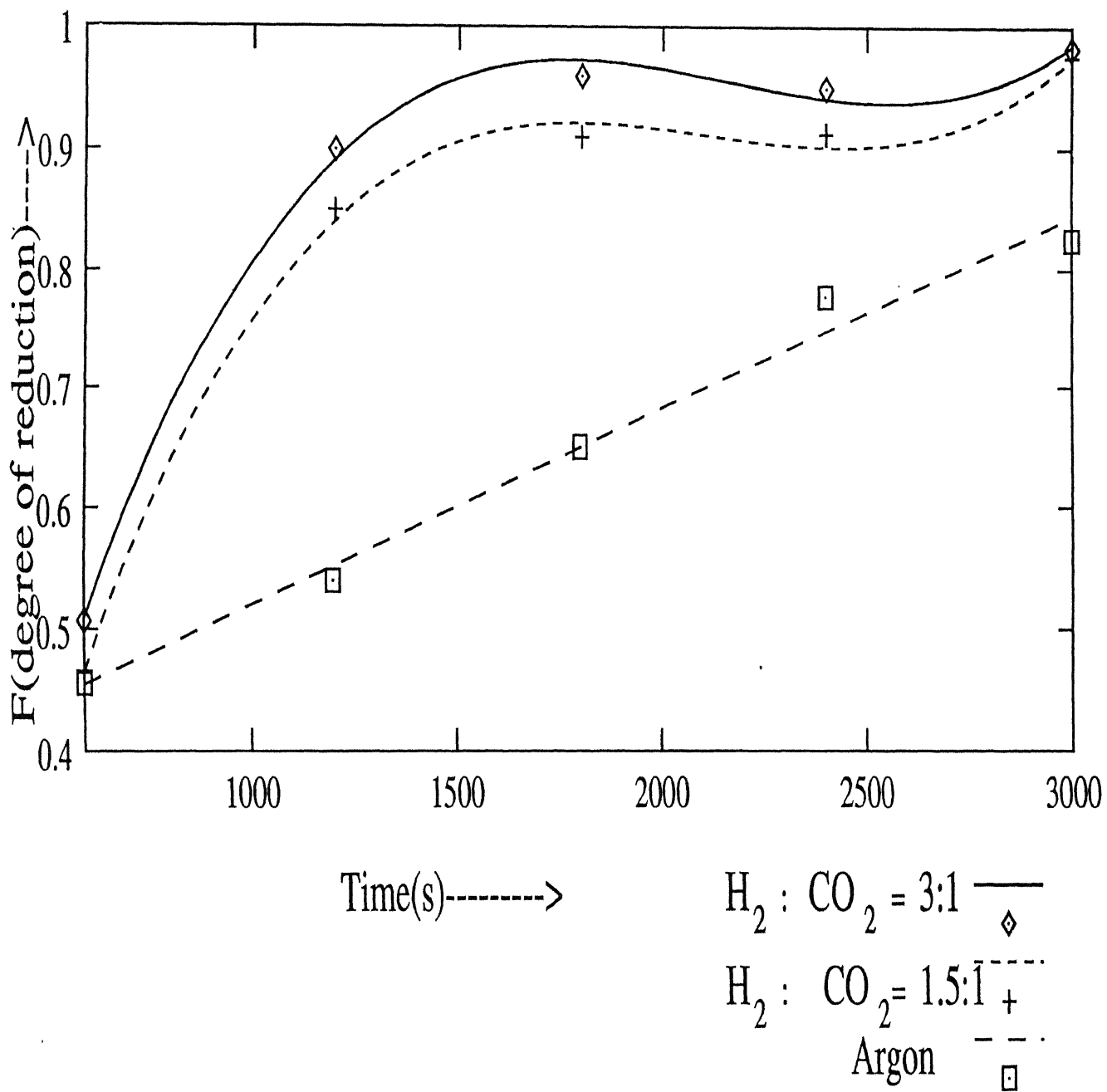
Figure 4.11: Variation of F with time for $Fe_2O_3/C = 4.5$ and big sample size at 1300K
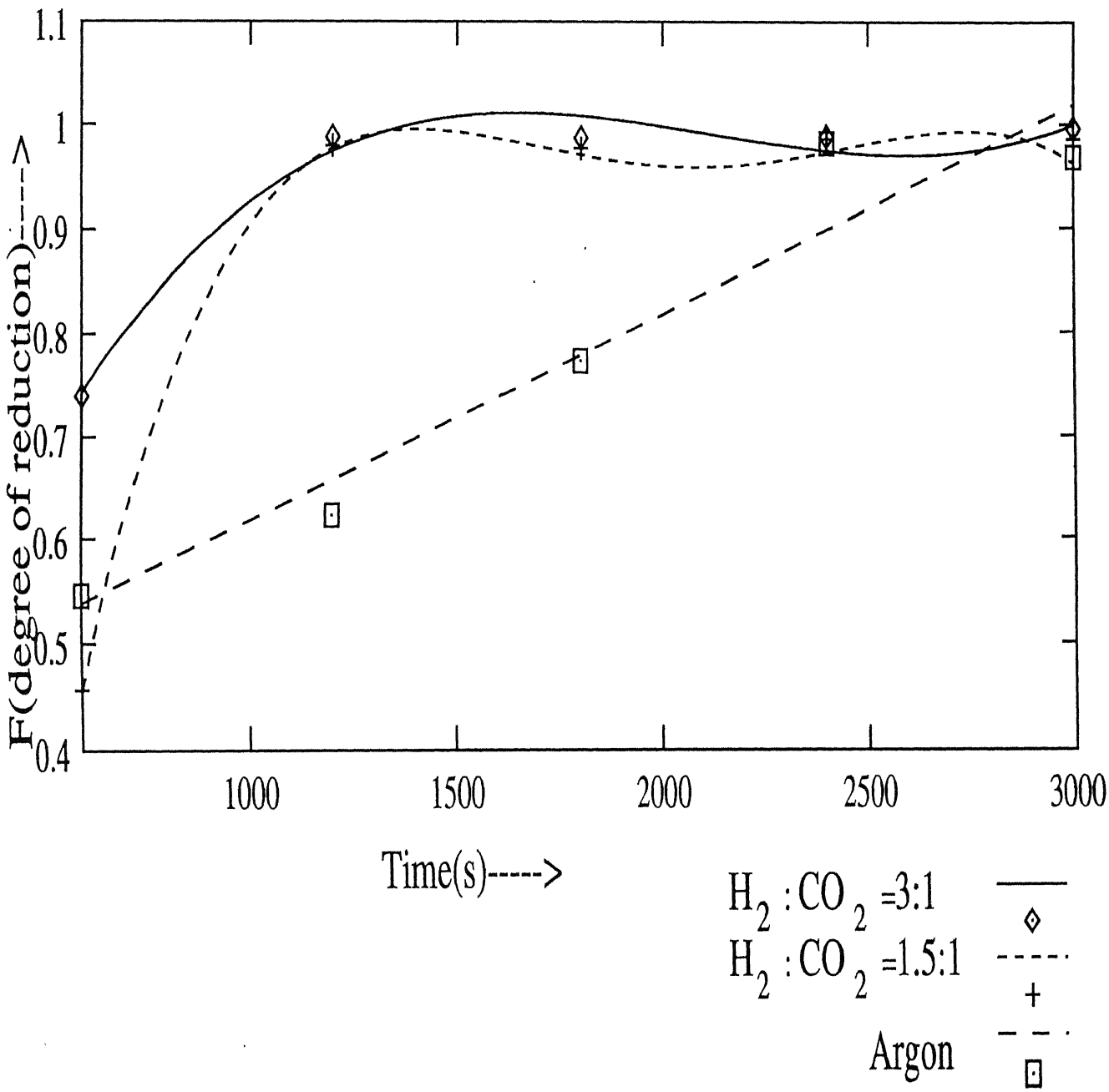
Figure 4.12: Variation of F with time for $Fe_2O_3/C = 3$ and small sample size at 1300K
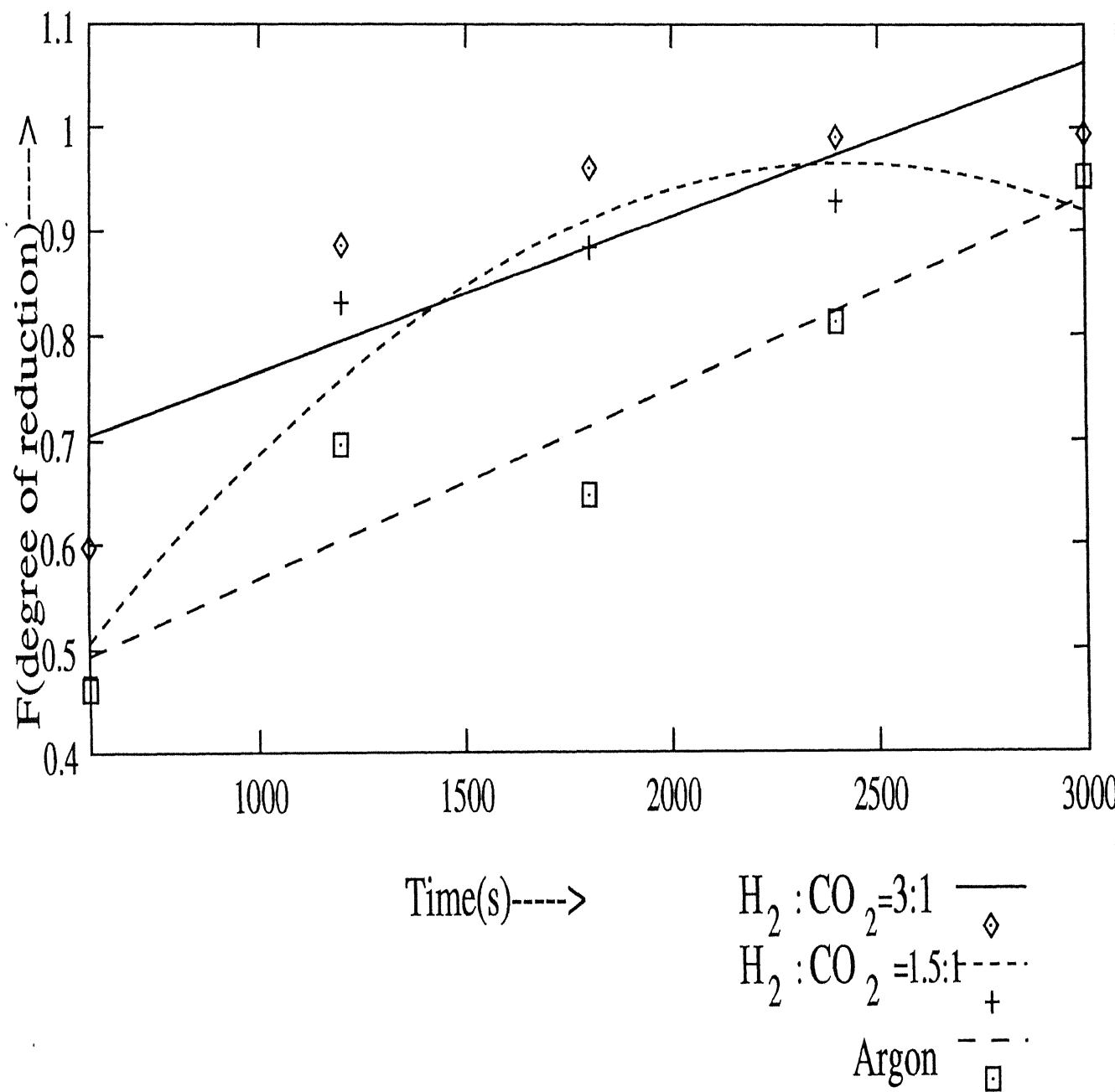
Figure 4.13: Variation of F with time for $Fe_2O_3/C = 4.5$ and small sample size at 1300K

expected. The values of F are lowest in argon. The gas mixture with H_2/CO_2 ratio of 1.5 also exhibited very high value of F, almost comparable to those with H_2/CO_2 ratio of 3 after some time of reduction. This is a very interesting feature and the only possible explanation is enhancement of the rate of gasification reaction by CO_2 and its consequent effect on degree of reduction.

4.2.5 Variation of degree of reduction with temperature

As Fig4.2 to 4.13 reveal, the effect of temperature on degree of reduction is not going to be the same at different times. In order to visualize influence of temperature therefore, it was decided to plot F at 2000 seconds as a function of temperature. Fig4.14 presents this for various experimental conditions. The curves in Fig.4.14 are based on polynomial fitted equations. The reason for choosing time equal to 2000 seconds is to avoid both initial and final times because

(i)initially the conditions are more complicated because the reactions are endothermic and it has been established in literature that it takes 400-600seconds approximately to attain steady state temperature and condition in the sample.

(ii)at 3000 seconds the quantity of carbon as well as Fe_2O_3 remaining in the sample will be small fractions. This is not representative of the sample. Hence 2000 seconds was chosen as the time.

Examination of Fig4.14 reveals the following behaviour patterns.

(i)F increases with temperature significantly for reduction under argon and under gas mixture with H_2/CO_2 ratio of 3. For H_2/CO_2 ratio of 1.5, however there was no increase from 1150K to 1250K. This shows that for this gas composition the oxidizing influence of the gas on wustite was dominant at this temperature range. However at 1300K the degree of reduction almost reached a value of 1. Again the possible explanation is rapid enhancement of gasification reaction rate above 1250K,consequent generation of CO and increase in F. This has already been stated earlier to explain F Vs.Time behaviour in this gas mixture at 1300K.

(ii)In argon the maximum value of F was about 0.8.

(iii)For gas mixture with H_2/CO_2 ratio of 3 the samples with Fe_2O_3/C ratio of 3 showed higher value of F as compared to that of Fe_2O_3/C ratio of 4.5(Fig.4.14). This may be due to excess carbon
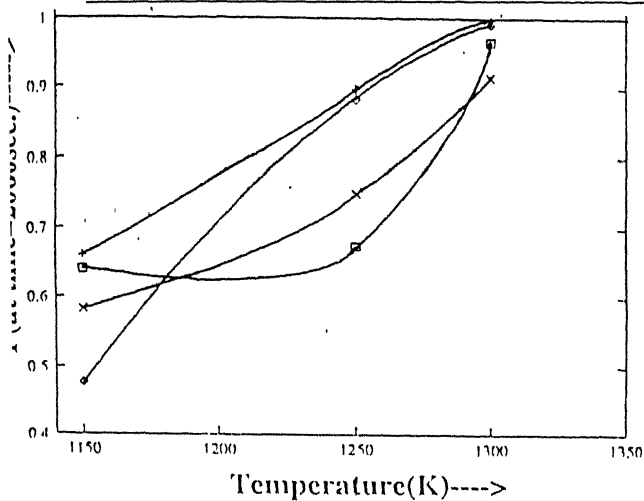
Gas composition $H_2:CO_2=3:1$

- ○ Mass ratio=3,sample size big
- + Mass ratio=3,sample size small
- □ Mass ratio=4.5,sample size big
- × Mass ratio=4.5,sample size small
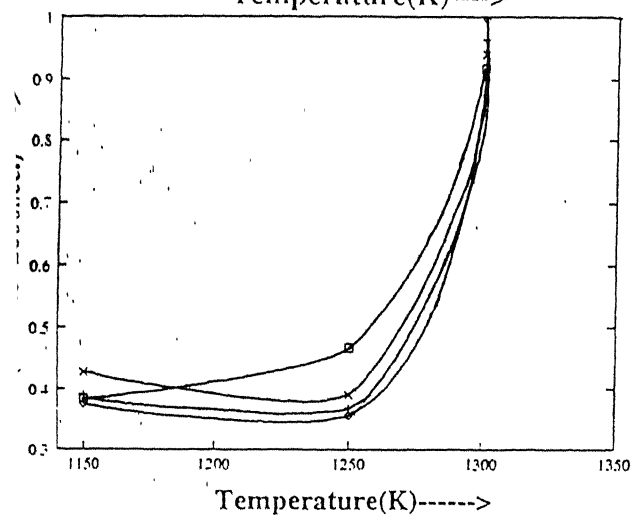
Gas composition $H_2:CO_2=1.5:1$

- ○ Mass ratio=3,sample size big
- + Mass ratio=3,sample size small
- □ Mass ratio=4.5,sample size big
- × Mass ratio=4.5,sample size small
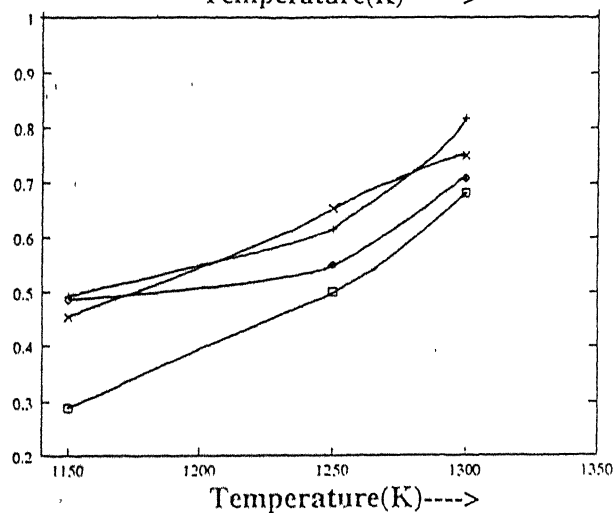
Gas composition=Argon

- ○ Mass ratio=3,sample size big
- + Mass ratio=3,sample size small
- □ Mass ratio=4.5,sample size big
- × Mass ratio=4.5,sample size small

Figure 4.14: Variation of F with temperatures at t = 2000 sec

in the sample. This behaviour pattern was observed only at 1300K for H_2/CO_2 ratio of 1.5 which matches with the earlier discussions.

(iv)Such generalizations were not possible for reduction in argon atmosphere.

As discussed earlier a high degree of reduction in H_2/CO_2 ratio of 3 is expected. However an interesting finding is that values of F at 1300K in gas mixture with H_2/CO_2 ratio of 1.5 and for Fe_2O_3/C ratio equal to 3,were almost equal to 1. Also for an increase in temperature to 1300K,large increase of F may be noted for this gas composition. Hence the only explanation for such high reduction is significantly high rate of gasification in this mixture and consequent increase of degree of reduction.

This observation is of relevance to reduction of composite pellets in industrial gaseous atmospheres containing H_2,H_2O,CO and CO_2. Thus even if the gas mixture is thermodynamically oxidizing to FeO,there is a likelihood of achieving very high degree of reduction if the temperature is high enough and the sample has some excess carbon.

4.2.6   Discussions on rates of reduction

A measure of rate of reduction is $\frac{dF}{dt}$. It is obtained by differentiating equation 4.3 and is represented by

$$\frac{dF}{dt} = b + 2ct + 3dt^2 + 4et^3 \tag{4.11}$$

In view of complex mechanism and kinetics as well as a range of behaviour patterns of F Vs. Time curves(Fig.4.2 to Fig.4.13) it is difficult to scientifically explain variation of $\frac{dF}{dt}$ with time. Hence only a few $\frac{dF}{dt}$ versus time curves(Fig4.15 to Fig4.17) are being presented to show various behaviour patterns. No explanation would be attempted.

Variation of $\frac{dF}{dt}$ with temperature may be represented by an Arrhenius type of equation, i.e,

$$\frac{dF}{dt} = Ae^{\left(\frac{-Q}{RT}\right)} \tag{4.12}$$

$$log\frac{dF}{dt} = logA - \frac{Q}{2.303 \times R \times T} \tag{4.13}$$

However there are the following difficulties.

(i)In Arrhenius equation,Q is known as activation energy,which is applicable only if there is one rate controlling step. This is not the case here. There are parallel reactions. Also,a single rate controlling step cannot be claimed . Hence Q here is simply a "Temperature Coefficient" and has no fundamental significance. However the magnitudes of Q do point out grossly about the rate controlling step and mechanism. Hence calculation of Q has been carried out.

(ii)Values of Q would depend on time. It was decided to calculate $\frac{dF}{dt}$ and Q for two times,viz,600second and 2100seconds only.

Table4.3 presents values of $log\frac{dF}{dt}$ at 1150,1250,1300K and values of Q for experiments in argon and gaseous mixtures of hydrogen and carbon dioxide. It may be noted that Q could not be calculated in some cases because $\frac{dF}{dt}$ values were negative and hence $log\frac{dF}{dt}$ could not be evaluated.

The values of Q were obtained by statistical regression fitting of data on the basis of Equation 4.13. There were very large scatter of data points in many cases. The range of values in many cases were large,in some cases it was small and in few it was negative.

Table 4.3: Log $\frac{dF}{dt}$ and Q at t=600seconds and t=2100seconds

Gaseous Environment	Fe$_2$O$_3$/C mass ratio	Sample size	Time(s)	Log dF/dt			Q (KJ/mole)
				1150 K	1250 K	1300 K	
H$_2$:CO$_2$=3:1	3:1	Big	600	-4.04	-3.52	-3.51	92.47
			2100	-4.04	-3.6	-	-
		Small	600	-3.77	-3.44	-3.209	105
			2100	-3.67	-3.69	-	-
	4.5:1	Big	600	-3.82	-4.02	-3.00	120.95
			2100	-3.82	-3.45	-	-
		Small	600	-3.52	-3.6	-3.82	-43.1
			2100	-4.15	-3.6	-3.82	79
H$_2$:CO$_2$=1.5:1	3:1	Big	600	-4.28	-3.47	-2.96	247.91
			2100	-5.18	-2.00	-	-
		Small	600	-4.56	-3.57	-2.73	336.68
			2100	-4.73	-3.97	-5.24	-45.77
	4.5:1	Big	600	-4.24	-3.7	-3.8	166.53
			2100	-4.24	-3.74	-	-
		Small	600	-5.07	-3.52	-3.29	354.13
			2100	-4.15	-3.9	-4.04	29.12
Argon	3:1	Big	600	-3.94	-4.32	-3.63	31.35
			2100	-3.94	-4.32	-3.56	47.59
		Small	600	-4.32	-3.53	-3.69	136.8
			2100	-4.09	-	-3.69	-
	4.5:1	Big	600	-3.65	-	-3.78	-
			2100	-3.98	-3.83	-3.78	38.71
		Small	600	-	-	-3.73	-
			2100	-3.74	-3.9	-3.7	-7.05
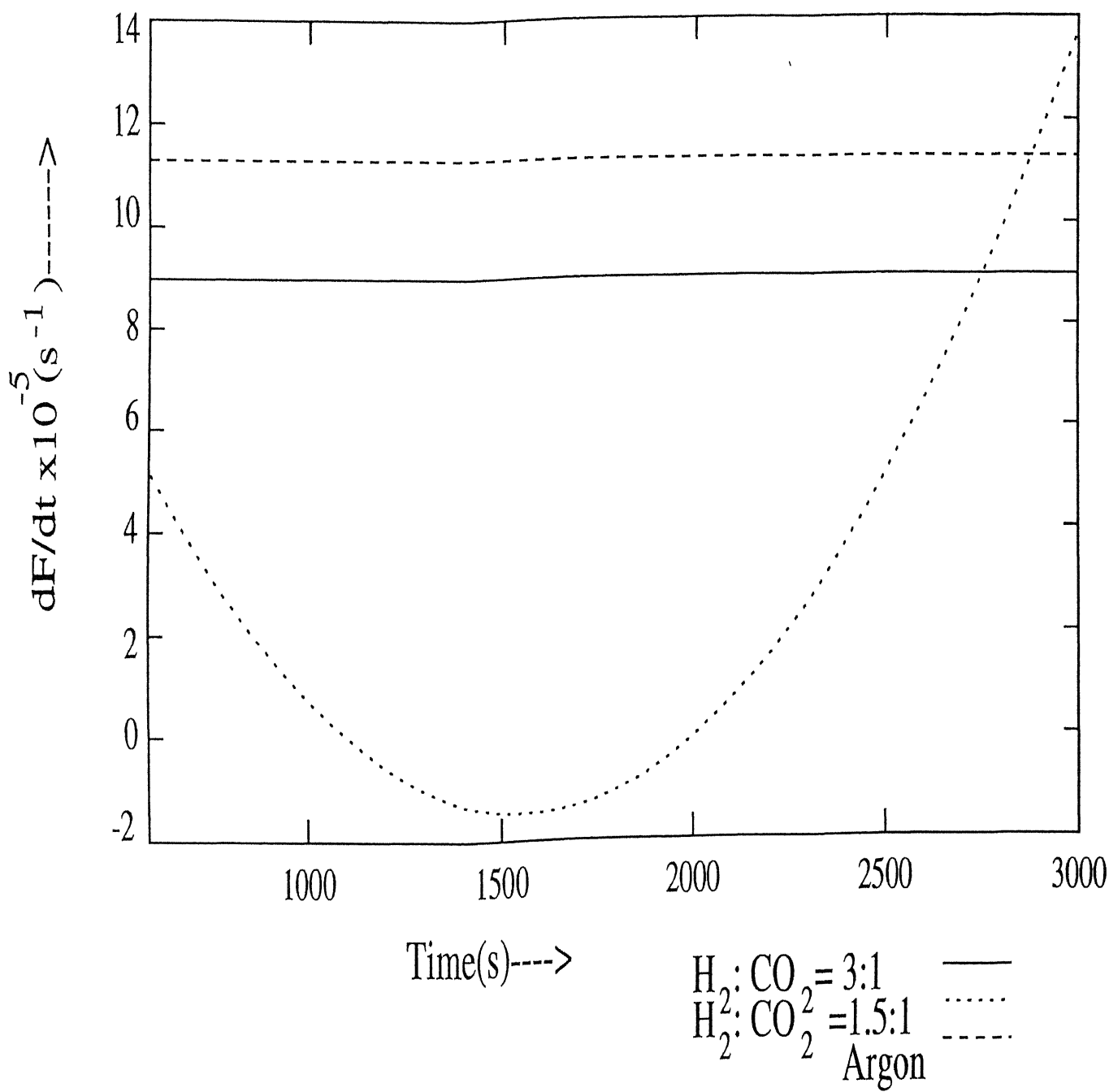
Figure 4.15: Variation of $\frac{dF}{dt}$ with time for $Fe_2O_3/C = 3$ and big sample size at 1150K
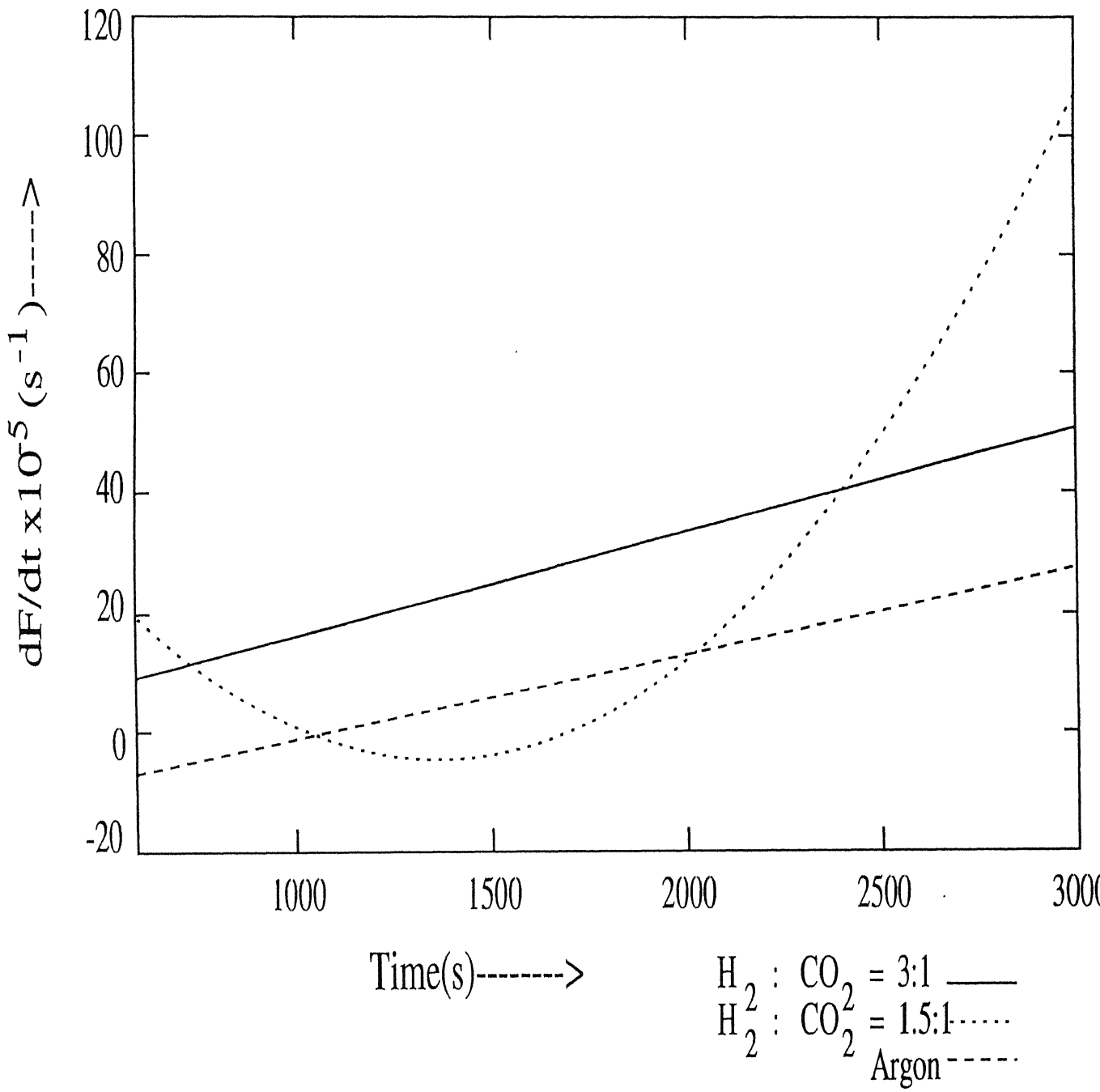
Figure 4.16: Variation of $\frac{dF}{dt}$ with time for $Fe_2O_3/C = 4.5$ and big sample size at 1250K
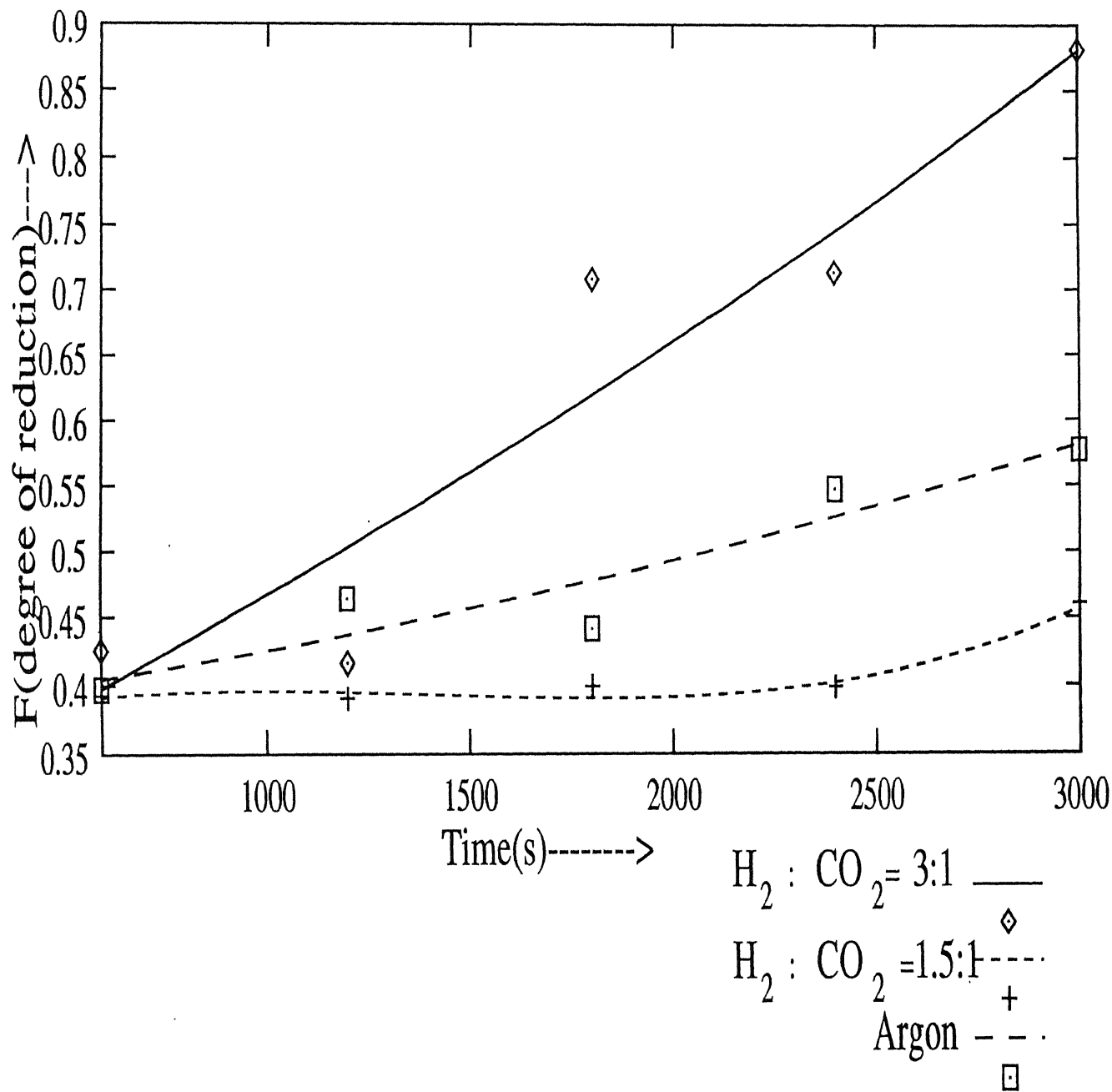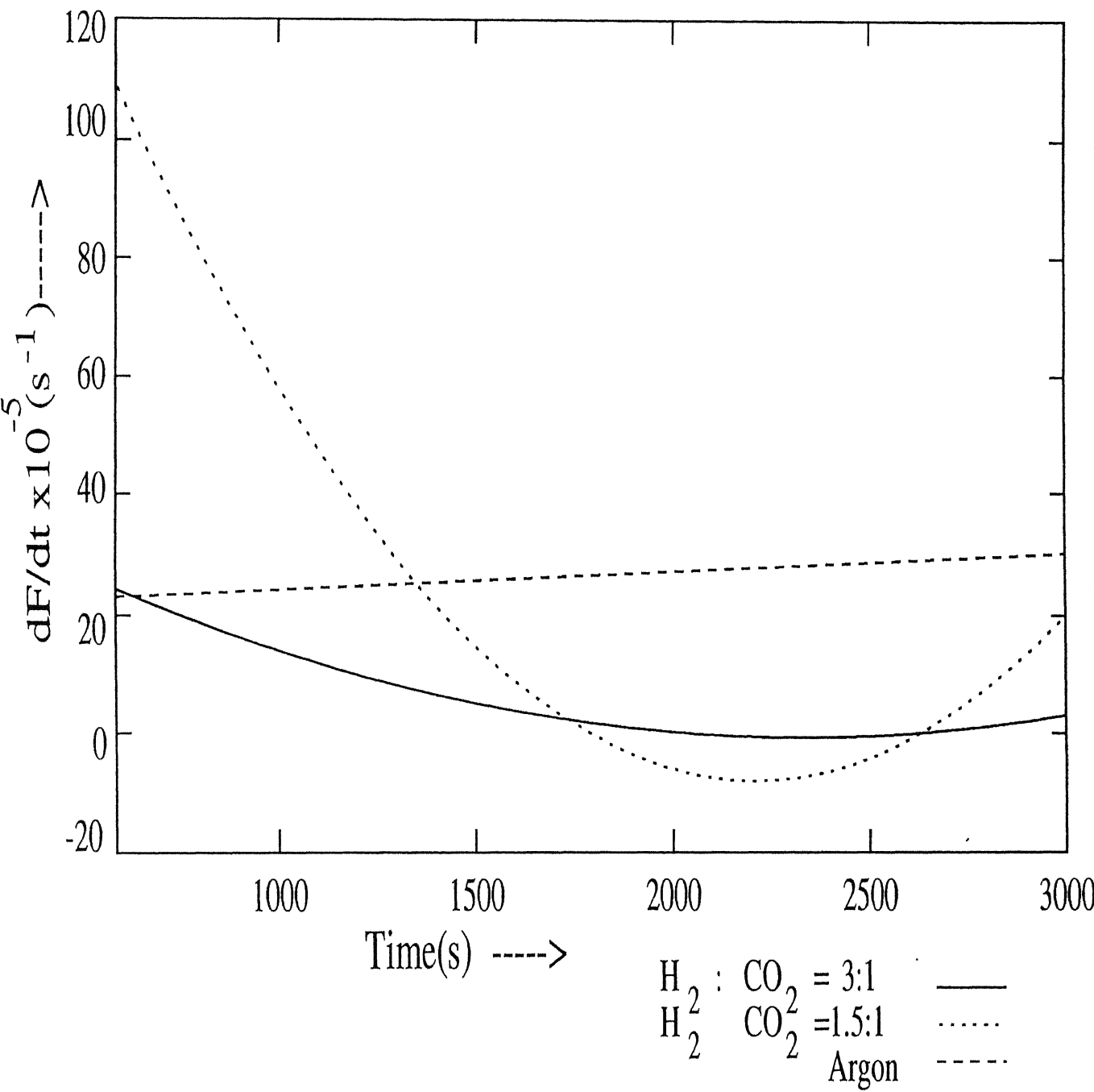
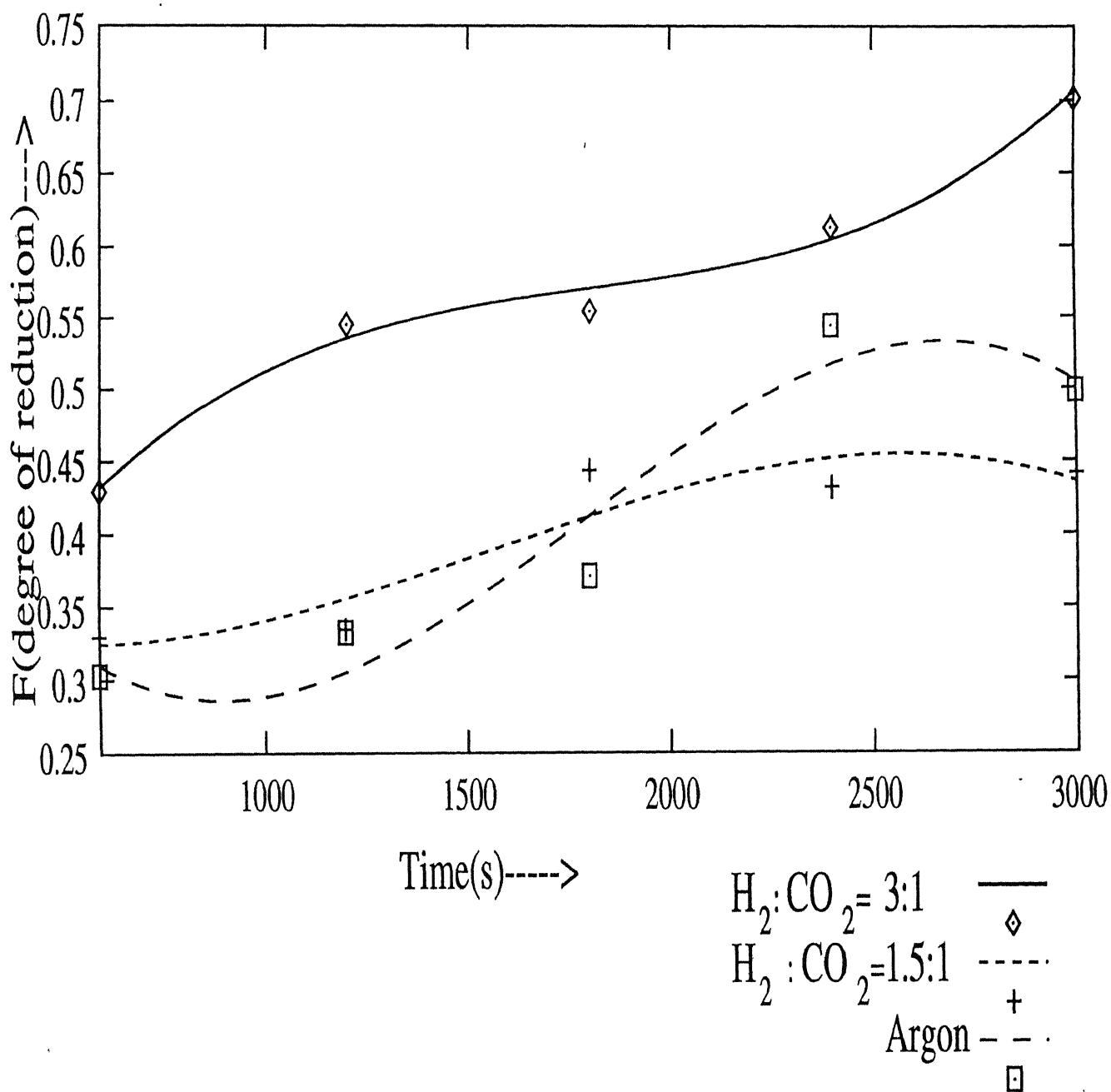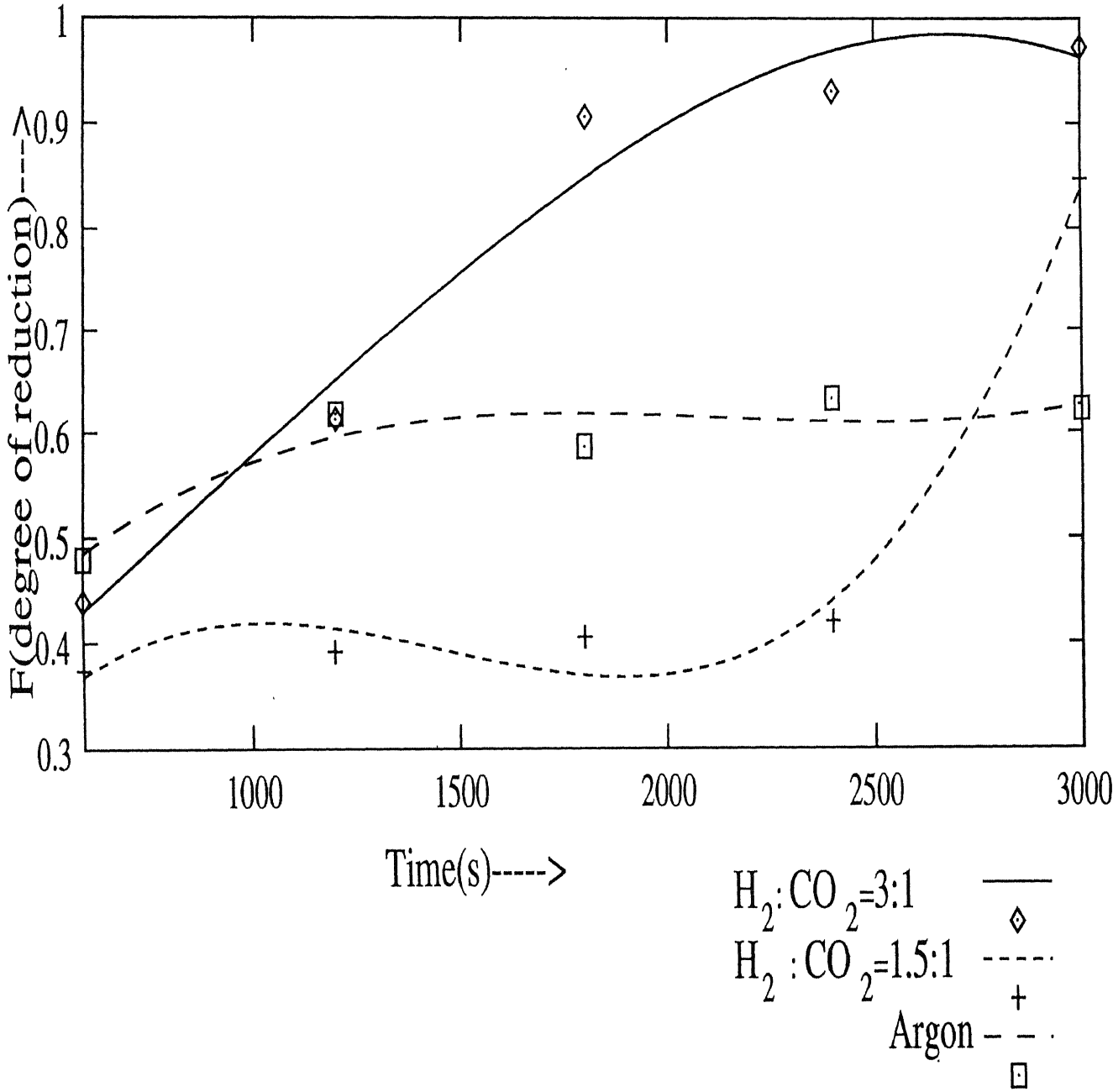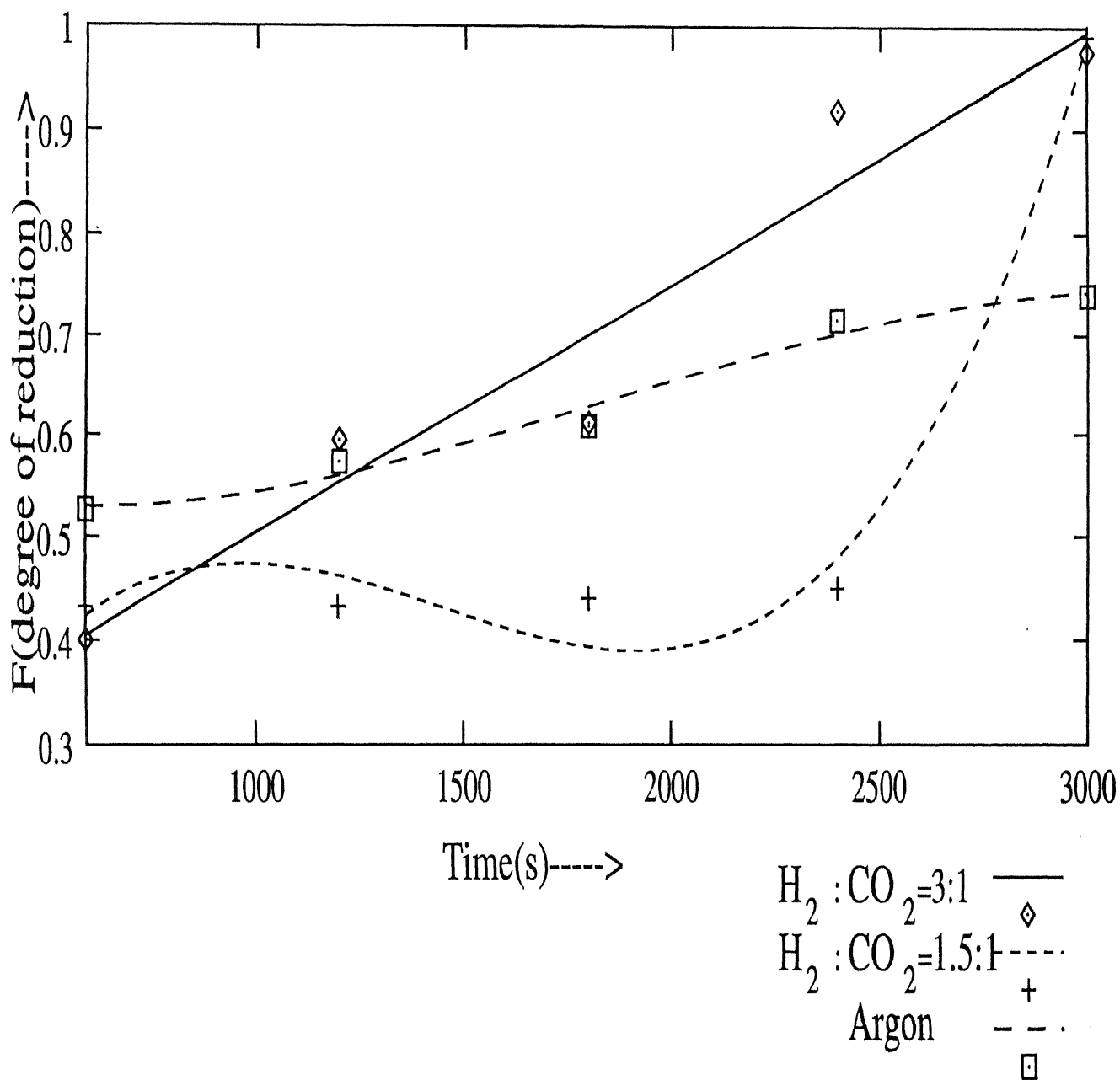Figure 4.17: Variation of $\frac{dF}{dt}$ with time for $Fe_2O_3/C = 3$ and big sample size at 1300K

4.2.7 Comparison of reduction by graphite with that by activated char

Reactivity of graphite is low. Deo[1] has carried out experiments similar to the present investigation with activated char as the solid reductant. Preliminary measurements have confirmed that the reactivity of char was about an order of magnitude larger as compared to that of graphite. In this section a comparison of reduction behaviour between graphite and activated char, has been attempted.

From industrial point of view the following parameters are of significance
(i) minimum time required to attain 90% reduction i.e.F=0.9. This time is designated as t_{90}. Maximum degree of reduction is designated as F_{max}, which means which means F at 3000seconds for this series of experiments.

Table4.4 presents values of t_{90} in seconds for both activated char and graphite. In some experiments 90% reductions were not obtained. Hence there are some blanks in the table. Table 4.5 presents values of F_{max}.

Fig 4.18 shows the comparison graphically for t_{90} for visualization of the comparison. Each point corresponds to the same experimental condition for graphite and activated char. Fig4.19 shows similar plot for F_{max}.

Generally,one would expect that t_{90} for activated char would be significantly lower as compared to those of graphite in view of higher reactivity of the former. However, in Fig4.18 it may be noted that value of t_{90} are comparable in lower time scale. In experiments where t_{90} were on larger side, the values are larger for activated char as compared to those for graphite.

So far as F_{max} is concerned the values should be larger for activated char as compared to those for graphite. However, the situation is just the reverse here also. Broad explanation for this anamolous behaviour are as follows.

(i) Graphite exhibits significant catalysis by reduced metallic iron[7] , thus leading to enhancement of rate. On the other hand coconut char did not exhibit significant catalytic effect[8, 10]. These have been reviewed in chapter 2 (section 2.2.3) . (ii) It may be noted from this table(Table4.4), 90% reduction were not obtained for reduction under argon except for graphite at 1300K. Therefore the role of reactive gases is important for F_{max} larger than 0.8 or so. This also may be explained by catalytic effect of metallic iron in presence of H_2, H_2O in the gas mixture.

From this, it may be tentatively concluded that reactivity of carbon does not seem to be of importance for reduction in reactive gas mixture. This is an important observation for industrial reduction of composite pellets.
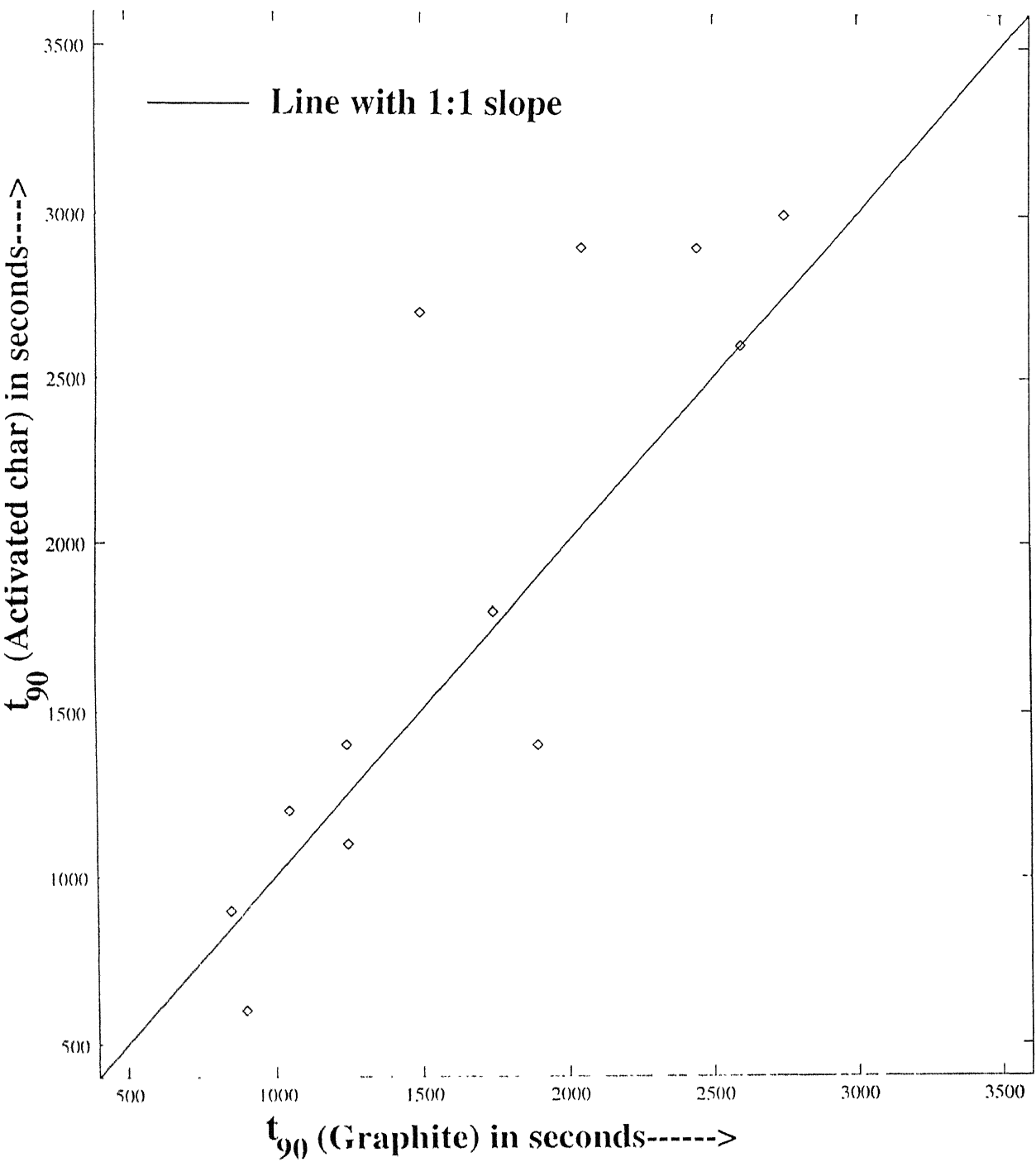
Figure 4.18: Comparison of minimum time to attain 90% reduction between graphite and activated char
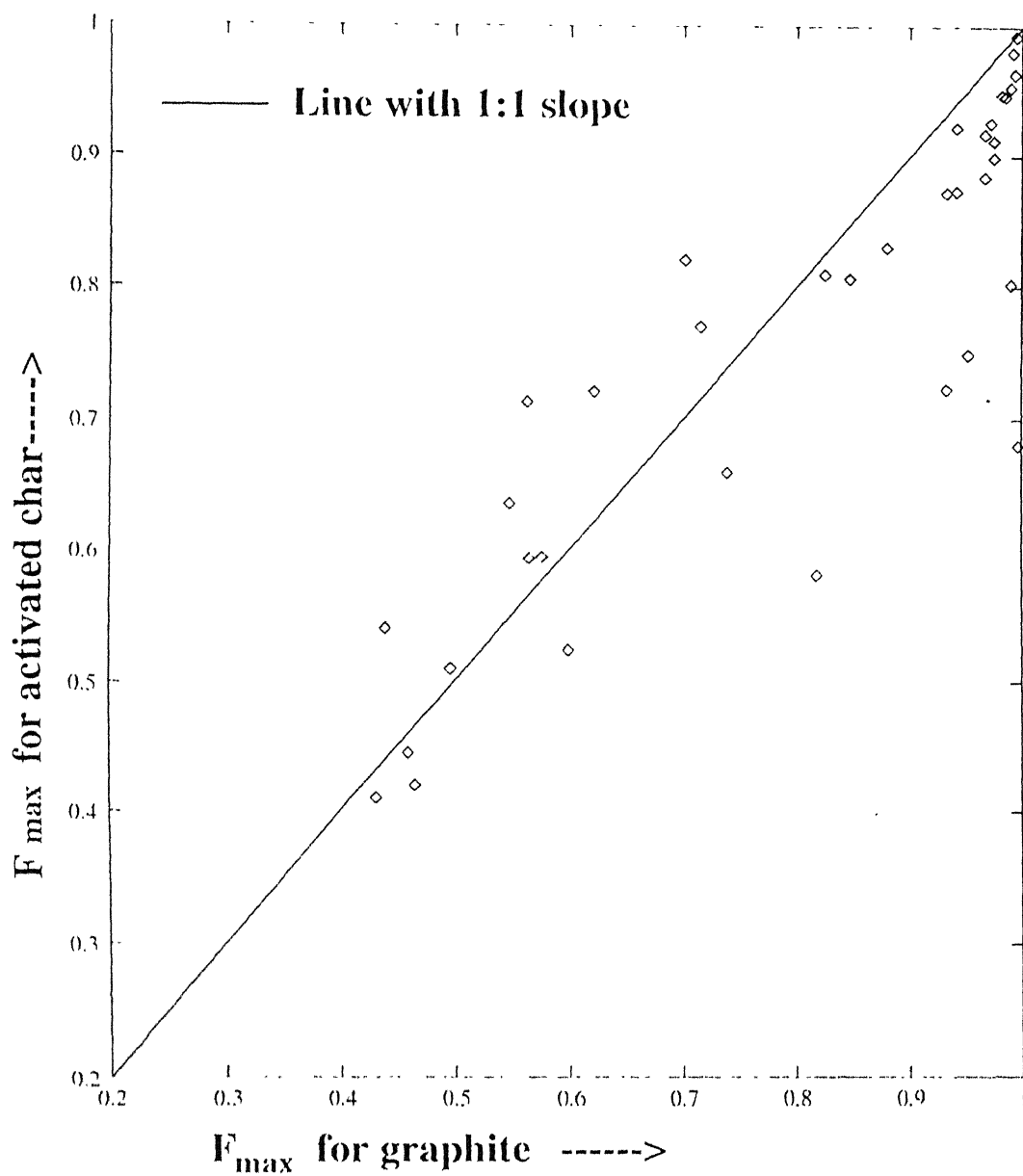
Figure 4.19: Comparison of F_{max}(i.e.F at t=3000seconds) for graphite and activated char

Table 4.4: Minimum time to attain F=0.9(t_{90}) with graphite and activated char

Temperature (K)	Gas composition	Fe_2O_3/C ratio	Sample size	t_{90} (sec).	
				Activated char	Graphite
1150	H_2:CO_2=3:1	3:1	Big	-	-
			Small	-	-
		4.5:1	Big	-	-
			Small	-	-
	H_2:CO_2=1.5:1	3:1	Big	-	-
			Small	-	-
		4.5:1	Big	-	-
			Small	-	-
	Argon	3:1	Big	-	-
			Small	-	-
		4.5:1	Big	-	-
			Small	-	-
1250	H_2:CO_2=3:1	3:1	Big	-	2200
			Small	2900	2050
		4.5:1l	Big	-	2650
			Small	2600	2600
	H_2:CO_2=1.5:1	3:1	Big	-	3000
			Small	-	-
		4.5:1	Big	-	2900
			Small	-	2900
	Argon	3:1	Big	-	-
			Small	-	-
		4.5:1	Big	-	-
			Small	-	-
1300	H_2:CO_2=3:1	3:1	Big	900	850
			Small	600	900
		4.5:1	Big	1100	1250
			Small	1400	1900
	H_2:CO_2=1.5:1	3:1	Big	1400	1250
			Small	1200	1050
		4.5:1	Big	2700	1500
			Small	1800	1750
	Argon	3:1	Big	3000	2750
			Small	2900	2450
		4.5:1	Big	-	-
			Small	-	2900

Note: Blank columns mean F = 0.9 were not attained in these experiments

Table 4.5: Maximum value of F(i.e. F at t=3000seconds) for graphite and activated char

Temperature (K)	Gas composition	Fe_2O_3/C ratio	Sample size	F_{max}	
				Activated char	Graphite
1150	H_2:CO_2=3:1	3:1	Big	0.635	0.548
			Small	0.83	0.88
		4.5:1	Big	0.58	0.818
			Small	0.82	0.701
	H_2:CO_2=1.5:1	3:1	Big	0.41	0.432
			Small	0.445	0.46
		4.5:1	Big	0.42	0.466
			Small	0.54	0.44
	Argon	3:1	Big	0.593	0.565
			Small	0.594	0.576
		4.5:1	Big	0.524	0.599
			Small	0.51	0.497
1250	H_2:CO_2=3:1	3:1	Big	0.872	0.933
			Small	0.926	0.972
		4.5:1	Big	0.884	0.967
			Small	0.912	0.975
	H_2:CO_2=1.5:1	3:1	Big	0.723	0.933
			Small	0.806	0.847
		4.5:1	Big	0.68	0.997
			Small	0.802	0.99
	Argon	3:1	Big	0.713	0.563
			Small	0.721	0.621
		4.5:1	Big	0.77	0.715
			Small	0.659	0.739
1300	H_2:CO_2=3:1	3:1	Big	0.98	0.992
			Small	0.993	0.995
		4.5:1	Big	0.948	0.982
			Small	0.964	0.994
	H_2:CO_2=1.5:1	3:1	Big	0.954	0.99
			Small	0.947	0.985
		4.5:1	Big	0.899	0.975
			Small	0.922	0.942
	Argon	3:1	Big	0.873	0.94
			Small	0.917	0.967
		4.5:1	Big	0.809	0.825
			Small	0.749	0.952

Chapter 5

SUMMARY AND CONCLUSIONS

(1)The experiments were conducted with mixtures of fines of blue dust and graphite at 1150K,125 and 1300K, and for times of 600,1200,1800,2400 and 3000 seconds respectively.

(2)The dried powder mixtures were taken in two sizes of cylindrical stainless steel crucibles (i.d 1.1cm and heights of 6mm and 1cm). A horizontal tube furnace was employed.

(3)The other variables were:
(a)inlet gas composition- argon, gas mixtures of hydrogen and carbon dioxide with H_2/CO_2 ratio equal to 3 and 1.5 respectively.
(b)Fe_2O_3/C mass ratios in the sample of 3 and 4.5 respectively.

(4)The total inlet gas flow rate in all atmospheres were kept at 4 cm^3/s(STP).

(5)The samples were weighed before introduction into the furnace and after taking out from the furnace.

(6)The degree of reduction was determined by subjecting the partially reduced samples through flowing hydrogen at 1023K for 1 hour. The weight loss in hydrogen was attributed to oxygen removal from unreduced iron oxide.

(7)F versus time data were fitted with polynomials by statistical regression.

(8)F versus time data for inlet gas of H_2/CO_2 ratio equal to 3 exhibited highest degree of reduction in most cases. The gas mixture with H_2/CO_2 ratio of 1.5, on the other hand, gave values of F which were lowest in several cases, and in some cases were found to be in the middle.

(9)At 1300K,almost complete reduction was observed even under gas mixture with H_2/CO_2 ratio equal to 1.5,although this gas is oxidizing to wustite from a thermodynamic point of view.

(10)In view of the complex mechanism and kinetics of reactions in the system ,$\frac{dF}{dt}$ values cannot be properly explained,although $\frac{dF}{dt}$ is a measure of rate.

(11)Temperature Coefficients(Q) were estimated from $\frac{dF}{dt}$ data. They exhibited wide range, and even negative values.

(12) Although, it was expected that activated char would reduce faster in view of its higher reactivity, it was not supported by experimental data. Catalytic effect of metallic iron on reactivity of graphite can explain this behaviour pattern.

Chapter 6

SUGGESTIONS FOR FUTURE WORK

(1)For better understanding of the kinetics of reduction of iron oxide with carbon,the following auxiliary measurements are desirable:

(a)measurement of reactivity of graphite in the gas mixtures,since the kinetics is dominantly controlled by gasification reaction,which again significantly depends on surrounding gas composition

(b)actual measurements of gas compositions in the hot zone of the reduction furnace

(c)measurement of temperature inside the sample should also be carried out during reduction in some experiments.

(2)Quantitative correlations on the basis of fundamental kinetics and the experimental data. If possible, mathematical modeling may be attempted.

(3) Similar experiments for other reductants,e.g. coal char, coke fines may be conducted.

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Appendix A

Experimental data in gas mixture of H_2/CO_2 ratio = 3:1

Table A.1:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	1.2715	0.2759	0.334					
	1200	1.1652	0.2528	0.42					
g3011h1b	1800	1.2767	0.2770	0.459	0.297	8.98			
	2400	1.1858	0.2573	0.531					
	3000	1.2435	0.2698	0.548					

Table A.2:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	1.3379	0.2903	0.392					
	1200	1.2211	0.2649	0.536					
g3012h1b	1800	1.298	0.2816	0.914	0.2647	4.44	0.0283	-0.00075	
	2400	1.1704	0.2539	0.904					
	3000	1.1741	0.2547	0.933					

Table A.3:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^1$
	600	1.1228	0.2436	0.856					
	1200	1.2989	0.2818	0.958					
g3013h1b	1800	1.1628	0.2523	0.987	0.6506	45	-0.0196	0.00028	
	2400	1.0367	0.2249	0.99					
	3000	1.1473	0.2489	0.992					

Table A.4:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	1.4264	0.3366	0.442					
	1200	1.5092	0.3561	0.543					
g4511h1b	1800	1.0758	0.2538	0.563	0.3398	15			
	2400	1.301	0.3070	0.708					
	3000	1.2962	0.3059	0.818					

Table A.5:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	1.3465	0.3177	0.496					
	1200	1.3015	0.3071	0.531					
g4512h1b	1800	1.4149	0.3339	0.523	0.5044	-8.734	0.86		
	2400	1.3028	0.3074	0.917					
	3000	1.2313	0.2905	0.967					

Table A.6:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	1.0462	0.2469	0.506					
	1200	0.9872	0.2329	0.899					
g4513h1b	1800	0.9262	0.2185	0.96	-0.362	196.28	-0.0939	0.0014	-0.00486
	2400	1.0169	0.2399	0.95					
	3000	1.0483	0.2473	0.982					

Table A.7:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	0.6918	0.1501	0.425					
	1200	0.6656	0.1444	0.416					
g3011h1s	1800	0.6136	0.1331	0.707	0.30094	15.187	0.00137		
	2400	0.5612	0.1217	0.712					
	3000	0.5879	0.1275	0.88					

Table A.8:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	0.6068	0.1316	0.439					
	1200	0.5686	0.1233	0.612					
g3012h1s	1800	0.649	0.1408	0.905	0.1897	126.42	-0.0627	0.00098	
	2400	0.5683	0.1233	0.93					
	3000	0.7069	0.1533	0.972					

Table A.9:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	0.6124	0.1328	0.74					
	1200	0.6506	0.1411	0.987					
g3013h1s	1800	0.7048	0.1529	0.986	-0.255	265	-0.2041	0.0067	0.008
	2400	0.4163	0.09033	0.987					
	3000	0.6475	0.1405	0.995					

Table A.10:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	0.6689	0.1578	0.428					
	1200	0.73	0.1722	0.545					
g4511h1s	1800	0.7032	0.1659	0.554	0.1899	55.5	-0.029	0.00053	
	2400	0.738	0.1741	0.613					
	3000	0.7474	0.1763	0.701					

Table A.11:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	0.7191	0.1697	0.400					
	1200	0.5718	0.1349	0.594					
g4512h1s	1800	0.7375	0.1740	0.611	0.2575	24.6			
	2400	0.6837	0.1613	0.918					
	3000	0.7484	0.1766	0.975					

Table A.12:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	0.5582	0.1317	0.597					
	1200	0.5104	0.1204	0.886					
g4513h1s	1800	0.5708	0.1347	0.96	0.6162	14.9			
	2400	0.6617	0.1561	0.99					
	3000	0.6601	0.1557	0.994					

Appendix B

Experimental data in gas mixture of H_2/CO_2 ratio $= 1.5{:}1$

Table B.1:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	1.0085	0.2188	0.373					
	1200	1.3372	0.2901	0.384					
g3011h2b	1800	1.0179	0.2208	0.376	0.3119	16.14	-0.0114	0.000243	
	2400	1.0998	0.2386	0.382					
	3000	1.1852	0.2571	0.432					

Table B.2:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	0.8872	0.1925	0.400					
	1200	0.9086	0.1971	0.414					
g3012h2b	1800	0.9761	0.2118	0.416	-0.0549	122	-0.0923	0.00208	
	2400	0.9546	0.2071	0.411					
	3000	0.9381	0.2035	0.933					

Table B.3:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	0.8454	0.1834	0.476					
	1200	1.0043	0.2179	0.929					
g3013h2b	1800	0.9499	0.2061	0.972	-0.467	212.5	-0.0997	0.0015	
	2400	0.9443	0.2049	0.991					
	3000	1.0378	0.2252	0.99					

Table B.4:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	0.9016	0.2127	0.319					
	1200	0.902	0.2128	0.324					
g4511h2b	1800	1.0733	0.2532	0.38	0.2698	5.742			
	2400	1.0027	0.2366	0.375					
	3000	0.96	0.2265	0.466					

Table B.5:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	1.423	0.3358	0.435					
	1200	0.999	0.2357	0.463					
g4512h2b	1800	1.1416	0.2694	0.46	0.172	72.7	-0.057	0.0014	
	2400	1.0763	0.254	0.564					
	3000	0.9416	0.2222	0.997					

Table B.6:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	0.9605	0.2266	0.463					
	1200	0.9874	0.233	0.85					
g4513h2b	1800	0.9801	0.2313	0.91	-0.3983	195.5	-0.095	0.0015	
	2400	0.8737	0.2061	0.912					
	3000	1.0958	0.2586	0.975					

Table B.7:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	0.5889	0.1277	0.392					
	1200	0.5398	0.1171	0.39					
g3011h2s	1800	0.5899	0.128	0.399	0.353	10.6	-0.0083	0.0002	
	2400	0.5411	0.1174	0.398					
	3000	0.5242	0.1137	0.46					

Table B.8:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	0.5384	0.1168	0.373					
	1200	0.549	0.1191	0.391					
g3012h2s	1800	0.4807	0.1043	0.405	0.0215	94.2	-0.0706	0.0016	
	2400	0.4471	0.097	0.419					
	3000	0.4818	0.1045	0.847					

Table B.9:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	0.409	0.0887	0.455					
	1200	0.4058	0.08805	0.979					
g3013h2s	1800	0.4504	0.0977	0.976	-1.69	577.8	-0.45	0.015	-0.018
	2400	0.4168	0.0904	0.985					
	3000	0.7045	0.1528	0.985					

Table B.10:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	0.5611	0.1324	0.329					
	1200	0.5619	0.1326	0.334					
g4511h2s	1800	0.464	0.1095	0.442	0.3591	-13.5	0.015	-0.00031	
	2400	0.424	0.10006	0.43					
	3000	0.5331	0.1258	0.44					

Table B.11:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	0.46	0.1085	0.431					
	1200	0.4247	0.1002	0.431					
g4512h2s	1800	0.4639	0.1094	0.439	0.0164	113.2	-0.088	0.002	
	2400	0.5946	0.1403	0.449					
	3000	0.457	0.1078	0.99					

Table B.12:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	0.3977	0.09385	0.474					
	1200	0.5165	0.1218	0.831					
g4513h2s	1800	0.5101	0.1203	0.883	0.1553	66.77	-0.0137		
	2400	0.5283	0.1246	0.929					
	3000	0.4704	0.111	0.942					

Appendix C

Experimantal data in argon

Table C.1:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	1.1477	0.249	0.269					
	1200	1.0398	0.2256	0.456					
g3011arb	1800	1.1053	0.2398	0.484	0.2603	11.3			
	2400	1.0131	0.2198	0.542					
	3000	1.1021	0.2391	0.565					

Table C.2:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	0.9963	0.2161	0.439					
	1200	1.1076	0.2403	0.483					
g3012arb	1800	1.0179	0.2208	0.534	0.4336	-3.65	0.009	-0.0002	
	2400	1.0484	0.2275	0.573					
	3000	1.1026	0.2392	0.563					

Table C.3:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	1.2445	0.27	0.396					
	1200	1.1294	0.245	0.437					
g3013arb	1800	1.2233	0.2654	0.612	0.223	21.46	0.0014		
	2400	1.2289	0.2666	0.943					
	3000	1.0699	0.2321	0.942					

Table C.4:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	1.3463	0.3177	0.215					
	1200	1.311	0.3093	0.252					
g4511arb	1800	1.274	0.3006	0.311	-0.0326	62	-0.041	0.0009	
	2400	1.2834	0.3028	0.324					
	3000	1.2947	0.3055	0.599					

Table C.5:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	1.243	0.2933	0.458					
	1200	1.2318	0.2907	0.444					
g4512arb	1800	1.2651	0.2985	0.494	0.528	15.5	0.0072		
	2400	1.2242	0.2889	0.551					
	3000	1.3082	0.3087	0.715					

Table C.6:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	1.3634	0.3217	0.455					
	1200	1.2575	0.296	0.539					
g4513arb	1800	1.275	0.3009	0.649	0.3568	16.3			
	2400	1.2397	0.2925	0.777					
	3000	1.2892	0.3042	0.825					

Table C.7:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	0.4815	0.1044	0.396					
	1200	0.6408	0.139	0.464					
g3011ars	1800	0.5903	0.128	0.441	0.3789	3.57	0.001		
	2400	0.5483	0.1189	0.546					
	3000	0.6063	0.1315	0.576					

Table C.8:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	0.48255	0.1047	0.479					
	1200	0.5046	0.1094	0.617					
g3012ars	1800	0.54	0.1171	0.585	0.2298	57.7	-0.028	0.00043	
	2400	0.5862	0.1272	0.631					
	3000	0.5277	0.1145	0.621					

Table C.9:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	0.4924	0.1068	0.545					
	1200	0.6683	0.14502	0.623					
g3013ars	1800	0.642	0.1393	0.772	0.4179	20			
	2400	0.5702	0.1237	0.981					
	3000	0.5577	0.121	0.967					

Table C.10:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	0.6554	0.1546	0.302					
	1200	0.7009	0.1654	0.332					
g4511ars	1800	0.6544	0.1544	0.371	0.5389	63.3	0.047	-0.00087	
	2400	0.536	0.1264	0.543					
	3000	0.6029	0.1422	0.497					

Table C.11:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	0.5882	0.1388	0.526					
	1200	0.6027	0.1422	0.572					
g4512ars	1800	0.627	0.1479	0.608	0.575	-15.9	0.0155	-0.00027	
	2400	0.5106	0.1205	0.714					
	3000	0.5537	0.1306	0.739					

Table C.12:

Exp. code	Time(s)	Ws(gm)	Wio(gm)	F(DoR)	a	$b \cdot 10^5$	$c \cdot 10^5$	$d \cdot 10^7$	$e \cdot 10^{11}$
	600	0.6077	0.1434	0.46					
	1200	0.6729	0.1588	0.696					
g4513ars	1800	0.6167	0.1455	0.646	0.3839	18.3			
	2400	0.6438	0.1519	0.812					
	3000	0.7053	0.1664	0.952					

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